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LOW TEMPERATURE FLUORINATION OF AEROSOL SUSPENSIONS OF HYDROCAR--ETC(U)

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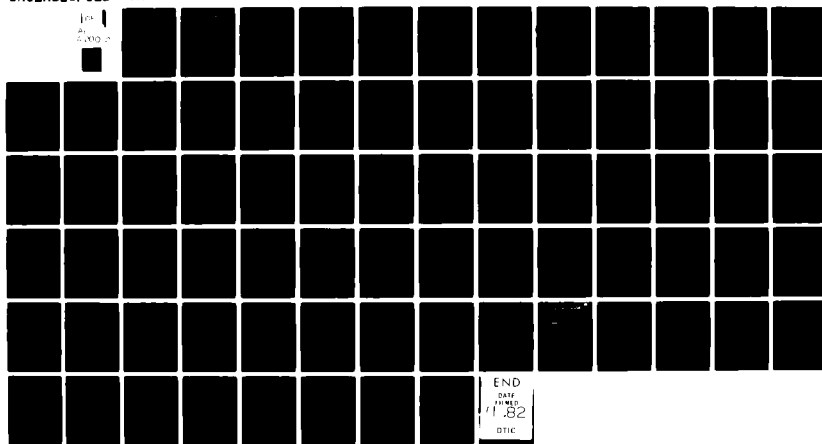
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Low Temperature Fluorination of Aerosol Suspensions of Hydrocarbons
Utilizing Elemental Fluorine

by

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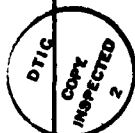
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THE
LOW TEMPERATURE FLUORINATION OF AEROSOL
SUSPENSIONS OF HYDROCARBONS
UTILIZING ELEMENTAL FLUORINE

by

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Lilly-Heller-Grossman and Mark L. Robin
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ABSTRACT

The extension of the aerosol fluorination technique to molecules possessing different hydrogen environments on the molecules has proceeded to include acyl halides, ketones, alkyl halides, amines and thioethers. Results on the fluorination of molecules with primary, secondary and tertiary hydrogens is also included as is the effect of admitting boron trifluoride into the aerosol direct fluorination of neopentane. The aerosol direct fluorination of ketones indicates the carbonyl group remains intact and the major product is the F-ketone, although in some instances acid fluorides result.

The use of photochemical excitation of the fluorination reaction is developed further and to date provides the most effective/efficient method for the complete conversion of hydrocarbons to perfluorocarbons. Preliminary optimization of reaction parameters has led to significant yield increases. Aerosol fluorination of larger less volatile molecules is proceeding and virtually no reduction in reactor efficiency has been noted.

INTRODUCTION

Aerosol direct fluorination is a new concept in direct fluorination taking advantage of the flow mobility and high surface area of a gaseous suspension of preferably crystalline particulates, preserving the advantages of static, fluorine concentration gradient, temperature gradient (LTG) reactors while overcoming their slowness and batch nature. A complete reference to aerosol fluorination can be found in the recent paper by Adcock, Horita and Renk in the journal of the American Chemical Society.⁽¹⁾ A recent review of gradient direct fluorination in general is also available.⁽²⁾

This report includes data which illustrates the highly efficient utilization of fluorine gas in photochemical perfluorination reactions. The aerosol process coupled with the photochemical reaction stage provides the first example of an effective-efficient process for the complete conversion of hydrocarbons to perfluorocarbons using photochemical excitation.

Photochemical Finishing of Aerosol Direct Fluorinations

The reaction of molecular fluorine with hydrocarbon molecules is a vigorous reaction needing little initiation. We have however documented in earlier reports the reduced reactivity of methyl group hydrogens as the number of geminal fluorine substituents is increased.⁽¹⁾ It seems safe to assume that the reduced reactivity of hydrogens in more highly fluorinated hydrocarbon molecules is general. This being the case, the inability of direct fluorination reactions to produce perfluorination in more complex hydrocarbons than the butanes prior to the LaMar and the Low Temperature Gradient (LTG) techniques of Lagow and Margrave are readily explainable.⁽³⁾ The major change introduced by these techniques was to separate the direct fluorination into stages separate in time. Low fluorine concentration and low temperatures when the hydrocarbon was low in fluorine content followed by high fluorine concentrations, higher temperatures as the hydrocarbon became more highly fluorinated. These techniques resulted in striking improvements in yields for direct fluorinations. These techniques were however slow and were batch processes. Improving the reaction efficiency required significant new developments. The Aerosol Fluorinator provided these innovations.⁽¹⁾ Among the significant improvements was conversion to a flow process. The requirements for a mobile reactant and control of the initial fluorine concentration however precluded the attainment of 100 percent fluorine concentration in the latter stages. It was this early inability to achieve near 100 percent fluorine concentration, preventing perfluorination in yields exceeding ten percent, which prompted us to seek methods to overcome this deficiency.

Photochemical finishing of aerosol direct fluorinations is now routinely used to achieve upwards of ninety percent conversions of hydrocarbons to

perfluorocarbons with highly efficient utilization of elemental fluorine. The use of only 1.1 times the stoichiometric ratio of fluorine to hydrocarbon produces near complete conversion to perfluorinated products. High yields depend primarily on the ability to significantly (50%-70%) fluorinate the hydrocarbon molecule prior to entry into the photochemical reaction stage.

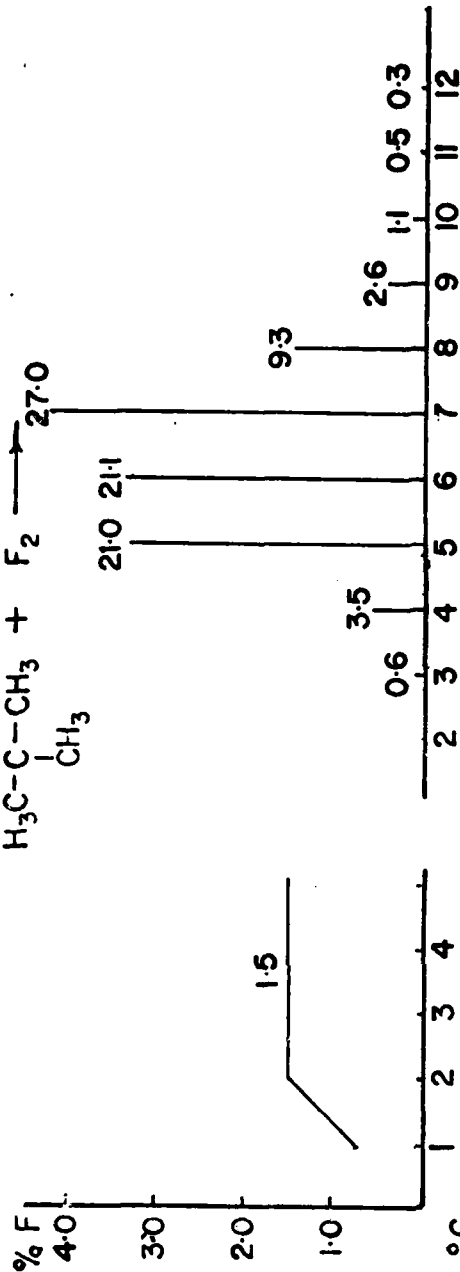
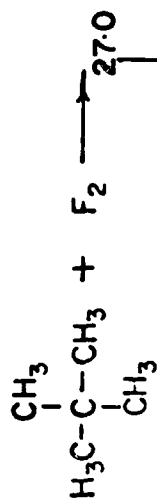
Product distributions produced by utilizing photochemical finishing are "anomalous" compared to "dark" fluorinations. Whereas the product distribution of substitution products varies continuously to higher degrees of fluorination as the fluorine concentration is increased in the dark reactions, use of the photochemical stage results in singular enhancement of perfluorination with only minor improvement of lower substitution product distributions (Figure 1). This effect is obviously due to excited hydrocarbon molecules being produced by fluorination which scavenge available fluorine molecules in a sustained sequence of reaction steps culminating in perfluorination. Such observations are compatible with a radical chain propagation mechanism modified to allow for reaction energy storage within the polyatomic hydrocarbon molecule.

This effect clearly explains the results reported by Nychka et. al. when he observed that hot tube, laminar flow reactions of ethane with a deficiency of fluorine produced only perfluoroethane and unreacted ethane.⁽⁴⁾ It also suggests why it is so difficult to limit direct fluorination to monofluorination; a difficulty we outline in a later section. The major "draw-back" to this photochemically initiated scavenging is our inability to limit a reaction with any repeatable success to a photochemically finished product one or two hydrogens short of perfluorination.

The photochemical reactor developed for this application is unique in that it establishes two stages of excitation. The reactor consists of a 550

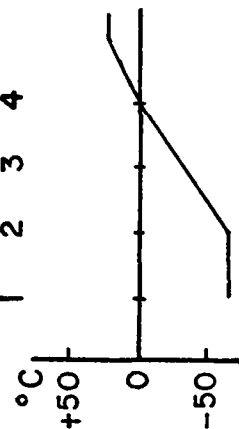
FIGURE 1

NEOPENTANE PRODUCT DISTRIBUTION

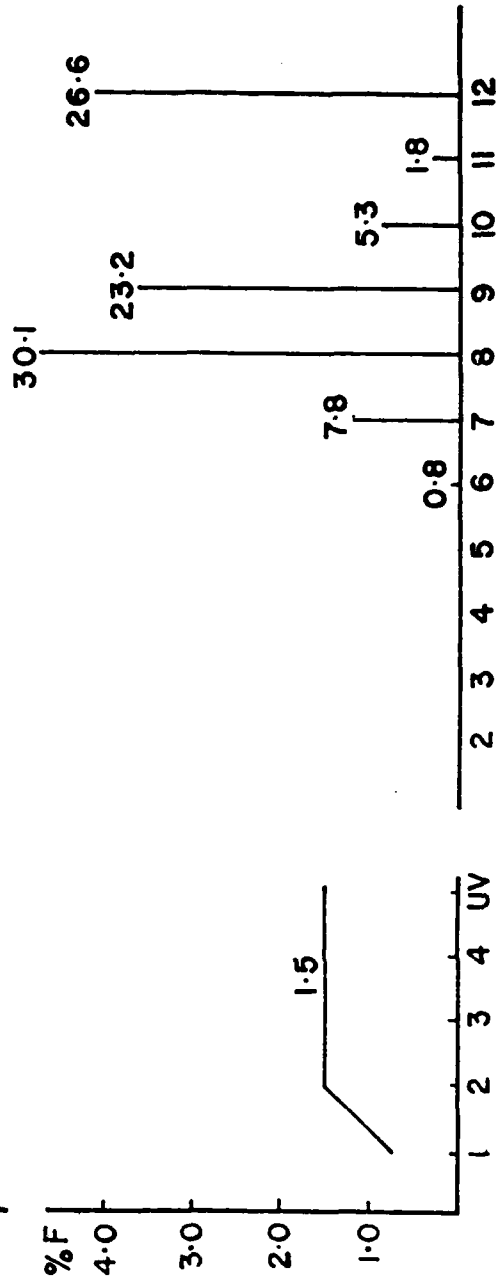


Hydrocarbon 4 millimoles/hour
 Fluorine: 96 millimoles/hour
 $\text{C}_5\text{H}_{12} + 2 \times 12 \text{F}_2 \xrightarrow{64 \text{ sec}}$

Temperature Gradient



With Ultraviolet Stage:



watt Hanovia lamp in a water cooled immersion well surrounded by 10 meters of 3/8 inch by 0.015 inch wall FEP Teflon tubing, a water coolant space, followed by a cylindrical pyrex filter surrounded by 15 meters of the FEP Teflon tubing. This unit is placed in a water filled, reflective stainless steel can which serves as the outer coolant chamber and reflector. Reactants passing into the reactor flow through the 15 meter pyrex filtered section are irradiated at wavelengths greater than 280 nm before passing into the 10 meters of quartz/water filtered ultraviolet which is limited by the transmission cut off of the FEP Teflon at 224 nm. All photochemical reactions were maintained at ambient water temperature which varied between 15°C and 30°C.

Because of the short residence times of hydrocarbon aerosols from generation to quenching at -196°C of from 0.25 to 4.0 minutes, the photochemical stage is technologically the simplest and currently the most efficient method of obtaining perfluorination at fluorine stoichiometries close to unity.

The photochemical stage, though extremely useful, is not a panacea. The inability to produce fluorocarbons in the 50% to 90% fluorinated range still requires dark reactions using high fluorine concentrations. To achieve these concentrations at constant carrier volume requires that a many fold excess of fluorine be added at later reaction stages. Efforts to increase fluorine concentration by selectively removing carrier gas in the latter stages of the reaction are currently being investigated.

AEROSOL DIRECT FLUORINATION OF VARIOUS HYDROGEN ENVIRONMENTS

Previous studies have shown that hydrogen on a tertiary carbon is more easily fluorine substituted than one on a secondary carbon and that a hydrogen on a secondary carbon is more easily fluorine substituted than one on a primary carbon.⁽⁵⁾ Since the above reactivities were determined for fluorinations in the liquid phase at -80°C , it was of interest to determine if aerosol direct fluorinations showed a similar pattern of reactivity. Since aerosol fluorinations are heterogeneous gas/solid reactions rather than solution reactions a molecule possessing primary, secondary and tertiary hydrogen environments would provide a more reliable comparison of relative hydrogen reactivities. Furthermore, the molecule should be sufficiently volatile to provide an ideally 2 millimole per hour throughput and for convenience have a minimum of isomers of the various substitution products. Such a molecule is 2,4-dimethylpentane. This highly symmetrical molecule has twelve identical primary hydrogens, two identical secondary and two identical tertiary hydrogens giving a $1^{\circ}:2^{\circ}:3^{\circ}$ ratio of 6:1:1.

In order to observe fluorination preference, monofluorination is desirable. Aerosol reaction conditions for the over twenty reactions carried out sought to limit fluorination by several methods which include the following:

1. reduction of the stoichiometry, the $\text{F}_2/\text{H.C.}$ ratio
2. reduction of the fluorine concentration in the helium carrier
3. reduction of the reaction-residence time
4. alteration of the fluorine concentration gradient
5. alteration of the temperature gradient

Various combinations of the above methods were used. At the mono- and di-fluorination level the most important variables are (1) the stoichiometry and (4) the fluorine concentration gradient. In none of the reactions could

substitution be completely limited to monofluorination. Even in those reactions having only 20% conversion of 2,4-dimethylpentane, difluoro-2,4-dimethylpentanes made up twenty percent of the fluorinated products. As the conversion increased to 94%, difluoro and higher substitution products made up 82% of the fluorinated products and the proportion of difluoro-2,4-dimethylpentanes was 1.75 times that of the monofluoro species. This pronounced tendency to undergo multiple substitution seems to be characteristic of low temperature, dark reactions of fluorine with hydrocarbons. Because of the ready controllability of the many reaction variables; the aerosol method clearly demonstrates this effect which is undoubtedly due to the formation of highly energetic molecules of hydrocarbon following reaction with a mixture of fluorine.

Despite the pronounced tendency toward difluorination information about the reactivities of hydrogen on the parent molecule toward fluorine can be extracted. Looking at reactions with the highest monofluoro/difluoro ratio and the highest monofluoro/total prod. ratio (rxns 4,8,12,13,15 Tables 1 and 2) the following preference for 1°:2°:3° is 9.3 :1.1:1 if all reactions are compared the preference is 11.4:1.1:1 compared to the statistical preference of 6:1:1. The experimental preference is not statistical and when normalized for the relative numbers of hydrogens becomes 1.55-1.90:1.1:1. Electronic effects if they operate at all would tend to favor 3° > 2° > 1° which is the order of electron density residing at those positions. It seems inescapable that steric shielding must play a rather large part in controlling the site preference for fluorine substitution. This is not to say that electronic effects do not matter, but only that the magnitude of differences in electron density between 1°, 2° and 3° hydrogens (carbons?) are not of meaningful significance in altering the position of fluorine attack.

TABLE 1
AEROSOL FLUORINATION OF 2,4-DIMETHYLPENTANES PRODUCT DISTRIBUTIONS-PERCENT TOTAL PRODUCT^a

REACTION NUMBER	MONOFLUORO			DIFLUORO								TRIFLUORO-HIGHER						PERCENT	
	3° A	2° B	1° C	D1	D2	D3	E	F	G	G1	H	I1	I2	I3	J	other	R ^a	REACTION	
4	3.1	3.0	30	.76	.67	.38	2.0	4.6	1.8	.08	3.3	.08	.08	.13	.12	1.2	49	51	
5	3.1	2.9	36	.40	.35	.20	2.8	8.2	3.6	.23	11.2	.38	.38	.67	41	0.5	25	75	
8	3.5	2.2	18	.88	.77	.44	1.5	1.9	0.7	-	0.8	0.08	.08	.14	-	0.5	68	32	
9	1.2	2.9	27	.52	.45	.26	1.8	4.3	2.1	.31	8.6	.62	.62	1.1	1.1	1.5	45	55	
10	1.4	1.8	14	1.7	1.5	.86	2.7	6.6	2.2	1.0	13.4	1.9	1.9	3.3	4.1	33	06	94	
11	2.3	2.1	21	1.5	1.3	.76	2.7	7.1	3.3	.74	15	1.5	1.5	2.7	3.9	17	13	87	
12	0.8	1.4	11	.20	.17	.10	.43	.75	.33	.05	1.2	.07	.07	.13	.30	.63	82	18	
13	1.0	1.6	11	.25	.22	.13	.49	.84	.33	.10	1.3	.06	.06	.10	.17	1.3	81	19	
14	1.6	2.5	24	.40	.35	.20	1.8	4.2	2.0	.56	8.9	1.0	1.0	1.8	2.4	10.4	35	65	
15	1.8	2.4	22	.28	.25	.14	.68	1.6	1.0	.17	3.9	.11	.11	.19	.87	1.5	63	37	
16	1.3	1.0	18	.35	.30	.17	1.1	3.0	2.1	.25	8.2	.22	.22	.38	2.2	1.5	59	41	
17	0.7	0.7	13	.26	.22	.13	.26	1.1	.87	.40	3.1	.07	.07	.13	.41	.12	78	22	
18	1.9	0.6	17	.30	.26	.15	.18	1.7	1.6	.21	5.7	.15	.15	.26	1.4	.66	68	32	
19	0.7	1.2	12	.21	.18	.10	.38	1.7	1.2	.56	5.1	.12	.12	.21	1.0	1.4	74	26	
20	0.7	1.1	8.4	.27	.23	.13	.75	.24	1.5	.77	7.1	.26	.26	4.0	2.2	2.2	71	29	

^aPrimarily unreacted 2,4-Dimethylpentane

TABLE 2

AEROSOL FLUORINATION OF 2,4-DIMETHYLPENTANES ISOMER PRODUCT DISTRIBUTIONS

DIFLUORO

MONOFLUORO

REACTION NUMBER	3° A	2° B	1° C	PERCENT MONOFLUORO	D1	D2	D3	E	F	G	GI	H	PERCENT DIFLUORO	TOTAL % REACTION
4	9	8	83	36.1	5.6	4.9	2.8	14.7	33.8	13.2	0.6	24.3	13.6	51
5	7	7	86	42.0	1.5	1.3	0.7	10.4	30.4	13.3	0.9	41.5	27.0	75
8	15	9	76	23.7	12.6	11.0	6.3	21.5	27.2	10.0	-	11.4	7.0	32
9	4	9	87	31.1	2.8	2.5	1.4	9.8	23.4	11.5	1.7	46.9	18.3	55
10	8	10	81	17.2	5.7	5.0	2.9	9.0	22.0	7.3	3.3	44.7	30.0	94
11	9	8	83	25.4	4.6	4.0	2.3	8.3	21.9	10.2	2.3	46.3	32.4	87
12	6	11	83	13.2	6.2	5.3	3.1	13.3	17.8	10.2	1.5	37.2	3.2	18
13	7	12	81	13.6	6.8	6.0	3.6	13.4	23.0	9.0	2.7	35.5	3.7	19
14	6	9	85	28.1	2.2	1.9	1.1	9.8	22.8	10.9	3.0	48.3	18.4	65
15	7	9	84	26.2	3.5	3.1	1.7	8.5	20.0	12.5	2.1	48.6	8.0	37
16	6	5	89	20.3	2.3	1.9	1.1	7.1	19.4	13.6	1.6	53.0	15.5	41
17	5	5	90	14.1	4.1	3.5	2.1	4.1	17.4	13.7	6.3	48.9	6.3	22
18	10	3	87	19.5	3.0	2.6	1.5	1.8	16.8	15.8	2.1	56.4	10.1	32
19	5	9	86	13.9	2.2	1.9	1.1	4.0	18.0	12.7	5.9	54.1	9.4	26
20	7	11	82	10.2	2.1	1.7	1.0	5.7	18.3	11.4	5.9	54.0	13.2	29
Average	8.8	9.8	81.4		4.35	3.77	2.18	9.43	22.15	11.69	2.66	43.4		
Standard ± Deviation	3.6	1.6	3.2		2.84	2.49	1.44	4.95	4.97	2.17	1.95	12.2		

TABLE 3

STATISTICAL PROBABILITY AND ISOMER DISTRIBUTIONS OF DIFLUORINATED 2,4-DIMETHYLPENTANES

COMPOUND	CALCULATED PROBABILITY	EXPERIMENTAL FRACTION $\pm$ Std. Dev.	EXP./Calc.	(code)
2,4-Bis(fluoromethyl)pentane (1,5-Difluoro-2,4-dimethylpentane)	0.300	0.434 $\pm$.122	1.45 $\pm$.41	DMP H
1,3-Difluoro-2,4-dimethylpentane	0.200	0.222 $\pm$.050	1.11 $\pm$.25	DMP F
1-Fluoro-2-fluoromethyl-4-methylpentane	0.150	0.117 $\pm$.022	0.78 $\pm$.15	DMP G
1,1-Difluoro-2,4-dimethylpentane	0.100	0.044 $\pm$.028	0.44 $\pm$.28	DMP D ₁
1,4-Difluoro-2,4-dimethylpentane	0.100	0.038 $\pm$.025	0.38 $\pm$.25	DMP D ₂
1,2-Difluoro-2,4-dimethylpentane	0.100	0.094 $\pm$.050	0.94 $\pm$.50	DMP E
2,3-Difluoro-2,4-dimethylpentane	0.033	0.022 $\pm$.014	0.66 $\pm$.44	DMP D ₃
3,3-Difluoro-2,4-dimethylpentane	0.008	----- a	-----	
2,4-Difluoro-2,4-dimethylpentane	0.008	----- a	-----	

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^aNot isolated, not found.

It can be argued that electronic effects may be decisive if their magnitudes are sufficiently large. Indeed our own data implies that this is the case. The most obvious example is the normalized relative reactivities of hydrogens on fluorinated neopentanes.⁽¹⁾ As previously discussed the order of hydrogen reactivity was $\text{CH}_3 > \text{CH}_2\text{F} > \text{CHF}_2$. This differential reactivity was attributed to both steric and electronic effects.

Additional support for electronic contributions comes from the isomer ratios of the various difluoro-2,4-dimethylpentanes, Tables 2 and 3. If one makes the assumption that fluorination occurs stepwise, the fluorination of 1-fluoro-2,4-dimethylpentane should yield 2,4-bisfluoromethylpentane (1,5-difluoro-2,4-dimethylpentane), 1-fluoro-2-fluoromethyl-methylpentane and 1,1-difluoro-2,4-dimethylpentane in a statistical ratio of 6:3:2. The experimental ratio of these three components is 10:2.7:1 or approximately 40:11:4 based on an average of fifteen reactions. It is clear from the data in Table 3 that the probability of fluorine attack on a primary hydrogen is 1.5 times that statistically predicted if the primary hydrogen is on a methyl group well removed from the site of prior fluorination; attack is only 78% as likely on an adjacent methyl group's hydrogen and only half (44%) as likely to attack a hydrogen on the fluorinated methyl group as statistically predicted.

The data in Table 3 is not so clearcut for the remaining difluoro-2,4-dimethylpentanes. For example 1,3-difluoro-2,4-dimethylpentane is 1.1 times the statistical probability and 1,2-difluoro-2,4-dimethylpentane is 94% however 1,4-difluoro- and 2,3-difluoro-2,4-dimethylpentanes are depressed to 38% and 66% respectively from their statistical probability. Each of these materials unlike the first group can arise from secondary or tertiary hydrogen substitution either in the monofluorination or the difluorination state

(Figure 2). Any conclusions, therefore, would be complicated by our inability to separate substituent effects operating in these two reaction paths.

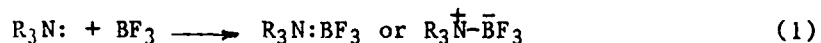
ACID/BASE CONSIDERATIONS IN AEROSOL DIRECT FLUORINATIONS

All of the prior aerosol fluorination work have used condensation type aerosol generation where reactant vapors are condensed onto preaerosol nucleating particulates composed of sodium fluoride. Although first considered as simply inert nucleating entities around which crystalline sublimates could condense, we are coming to realize that the particulates may also chemically affect the course of the fluorination reaction. If one were to view the gas matrix as a solvent of sorts, the endogenous hydrogen fluoride produced during fluorination of a hydrocarbon would produce an "acidic" environment, or gas solution. This endogeneous hydrogen fluoride might well influence the fluorination reaction by combining with organic intermediates etcetera. If this were the case, by a "solvent system" definition these sodium fluoride particles would be reacting with the hydrogen fluoride producing the less acidic bifluoride ion, neutralize this acidity and alter any reactions previously affected by it. It is also possible that fluoride ion might affect the reactivity of molecular fluorine itself. In fact an early patent claimed to have discovered a catalytic effect by metal fluorides on the direct fluorination reaction.⁽⁶⁾ One might speculate that a weak charge transfer complex analogous to the I_3^- ion might be operating to alter the reactivity of elemental fluorine. Although such a complex would be expected to have only transient stability at best, the presence of such an intermediate could alter fluorine reactivity significantly in polar or electrophilic systems. Support for such a complex might be obtained by Raman, and Visible-Ultraviolet spectroscopy. So far only very subtle differences between LTC (acidic) and Aerosol (basic) reactivities have been noted. There are however significant differences between either of the above and Simons electrochemical process which uses a very acidic medium although one would not like to weigh in with any closer comparisons.

Since we are now aware of the potential effects of altering the acidity of the system, we chose to approach the development of a mixer type aerosol generator with a view toward comparing the chemical effects as well as simply the physical aspects of adduct formation.

The mixer type aerosol generator is based on the idea that adducts generally have lower volatility and significantly different physical and chemical properties than either of their components. For example, both ammonia and boron trifluoride are low boiling gases however their adduct is a solid (m.p. 163°C).⁽⁷⁾ To generate a separate condensation aerosol of either of these components is difficult, but by bringing the two components together either with or without a nucleating-particle-laden carrier a rapid condensation occurs. Thus we are embarking on a set of experiments in which aerosols are generated between Lewis bases (amines, ketones, alcohols, aldehydes, ethers, etc.) and boron trifluoride.

Examination of the electronic structure of an adduct immediately presented us with many unanswered questions. Adduct formation is in effect a one electron transfer from the base to the Lewis acid. This transfer results in formal charging in the adduct (Eq. 1).



If, as our data with methyl groups in neopentanes⁽¹⁾ suggest, the fluorine reactivity toward methyl groups of: $CH_3 > CH_2F > CHF_2$ results from electronic rather than steric effects,⁽¹⁾ we should expect that $(CH_3)_3N$ should be considerably more reactive toward fluorine than $(CH_3)_3N:BF_3$. Our preliminary experiments clearly suggest this to be the case. A rationale for this behavior exists in the literature.⁽⁸⁾ Neil Bartlett has demonstrated the high reactivity of anionic (electron rich) species with both molecular and atomic fluorine. He further documents the very low reactivity of

fluorine with cationic species even at high pressures and temperatures.⁽⁸⁾ Furthermore the presence of boron trifluoride in the reaction stream should alter the acidity of the gaseous "solvent" by virtue of the fact that hydrogen fluoride acidity should be enhanced and fluoride ion should be complexed to form tetrafluoroborate ion. The high acidity of anhydrous HF especially in the presence of BF_3 should result in protonation of basic hydrocarbons leading to cationic species and low reactivity by fluorine. To correlate these various effects it was decided that the effects of boron trifluoride on the fluorination system aside from adduct formation with reactant Lewis bases should be investigated. The results outlined in the following section show that boron trifluoride has a subtle but still significant effect on the fluorination of neopentane under conditions that are essentially identical except for the presence of the Lewis acid.

NEOPENTANE/ BF_3 REACTIONS

For the reactions of neopentane and elemental fluorine in the presence of boron trifluoride, a dual inlet aerosol generator was employed. Initially a run was made with this aerosol generator using a small flow of helium (ca. 3cc/min) through the BF_3 inlet; the new generator had little or no effect on the product distributions, as seen by comparison to runs employing the single inlet aerosol generator.

Reactions were run with neopentane and fluorine in stoichiometric amounts (neopentane 2 mmole/hr, fluorine 24 mmole/hr). The BF_3 flow in all reactions was ca. 3cc/m (8 mmole/hr); lower BF_3 flows were not measurable due to the lower detection limits of the rotameters. Higher flows of BF_3 severely retarded the reaction promoting tar and oil formation.

The reactions performed in the presence of UV radiation showed a slight shift of the product distribution towards the perfluorinated product (72.4%

F-neopentane with no BF_3 ; 82.8% F-neopentane with BF_3) (Figure 3). The reactions not employing UV radiation showed a slight shift in the product distribution toward the more fluorinated product (Figure 4). In the presence of BF_3 the maximum occurs at the octafluoro or nonafluoroneopentane. The product yields did not appear to be affected by the presence of BF_3 in the system. Comparing two typical runs: Rxn. 16 (no BF_3) 547 mg of product were collected in the -110° trap; for Rxn 11 (BF_3), 519 mg of product were collected in the -110° trap.

FIGURE 3
PHOTOCHEMICALLY FINISHED
NEOPENTANE/BF₃ PRODUCT DISTRIBUTIONS

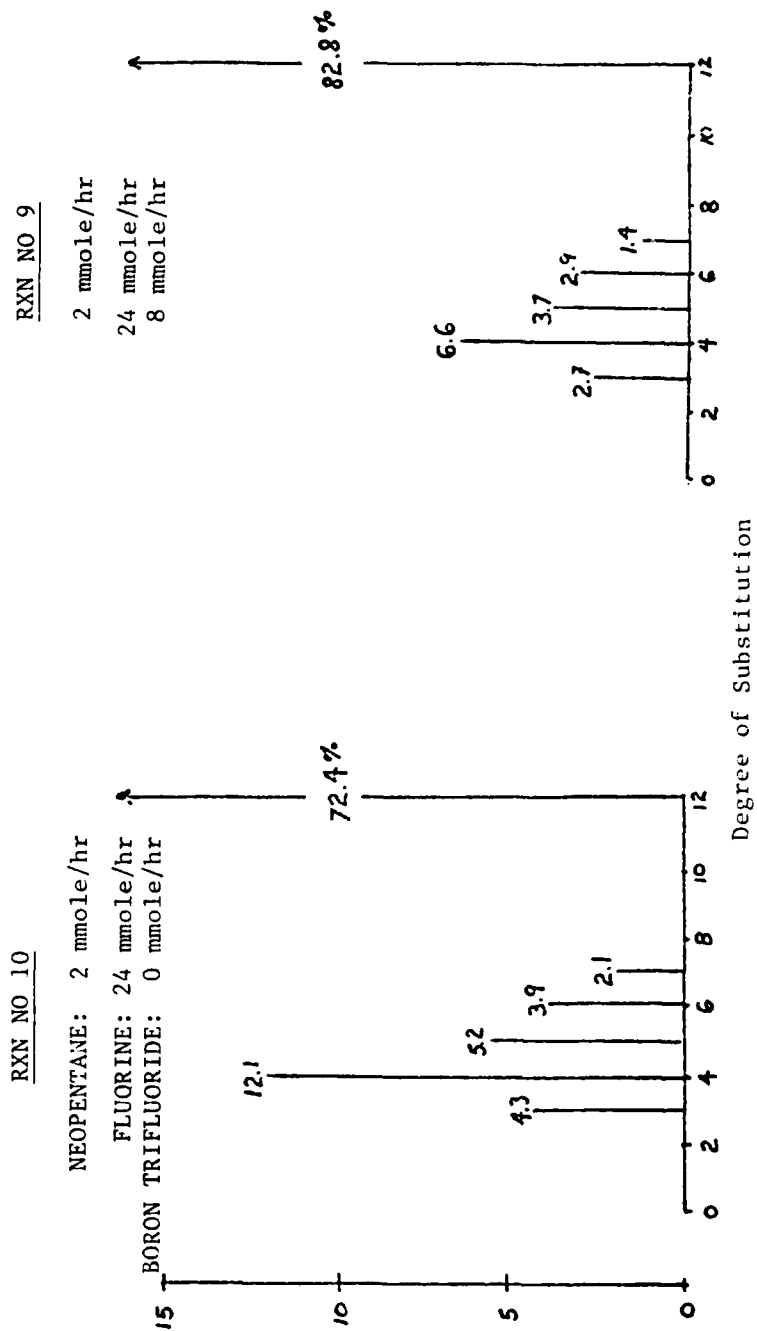
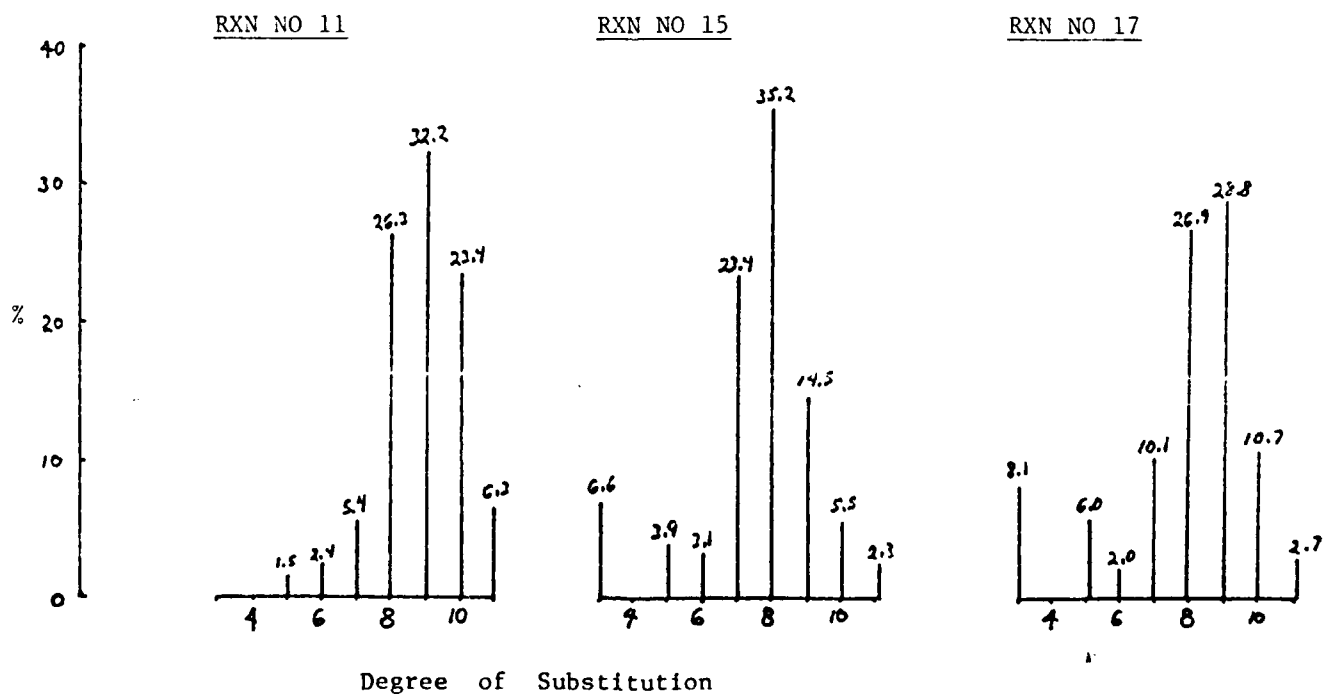
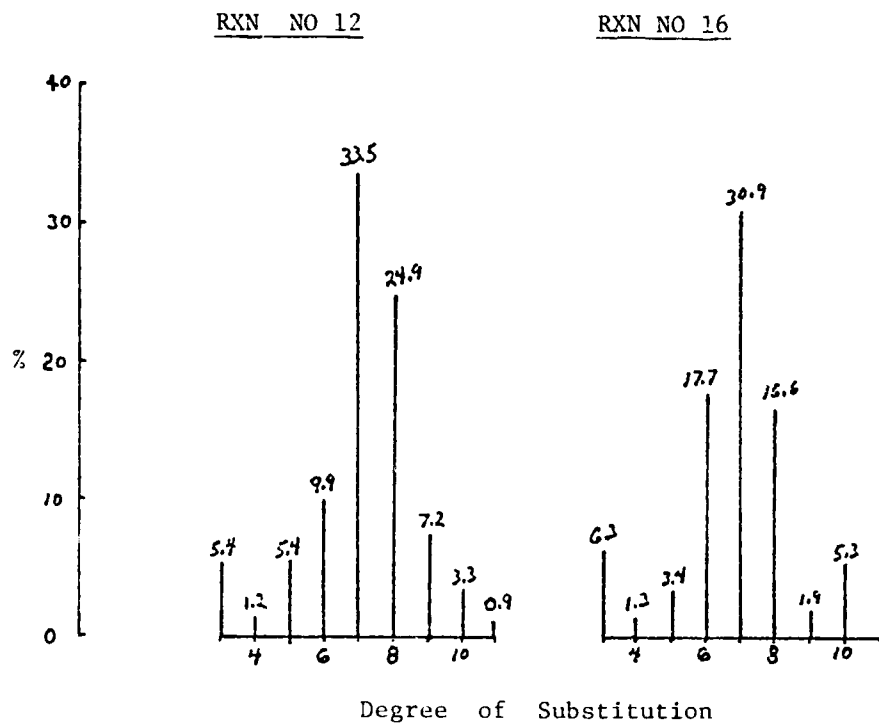


FIGURE 4

NONPHOTOLYSED NEOPENTANE / BF_3 PRODUCT DISTRIBUTIONS

AEROSOL DIRECT FLUORINATION OF ALKYL HALIDES

Alkyl Chlorides: The ability to retain a substituent on a hydrocarbon chain that can be a site for later reaction would be desirable. The most likely halogen substituent to survive direct fluorination would be chlorine. Although the reactivity of this substituent is limited, Schack and Christi have shown that chlorines can be substituted by so called "positive halogen" reagents, i.e. hypochlorites.⁽⁹⁾ Other possible reactions include dechlorination, dehalogenation, dehydrohalogenation. The dechlorination, replacement by hydrogen, is easily accomplished by the relatively expensive tri-n-butyltin hydride.⁽¹⁰⁾ However, we have discovered a cheap readily available reagent: reflux of F-alkyl chlorides with zinc/dioxan results in dechlorination. The hydrogen source is presumably dioxan. Zinc/dioxan will also form olefins from beta-dichlorides, other conditions permitting.⁽¹¹⁾ The ability of F-alkyl chlorides to capture electrons which result in an anion-radical which eliminates a chloride ion forming a radical, suggests that metallation of F-alkyl chlorides might be induced to occur under suitable conditions.⁽¹²⁾

Neopentyl Chloride-Neopentyl chloride prepared by the method of Wiley, et. al.⁽¹³⁾ was fluorinated to F-neopentyl chloride in yields of 74%. The product distribution of F-neopentyl chloride was 79.6% (glc assay) of the total product collected. The neopentyl group which is exceptionally easy to fluorinate by the aerosol method, is potentially useful as a biological probe and as a precursor for reagents containing the F-tert-butyl group.⁽¹⁴⁾

n-Butyl Chloride- 1-Chlorobutane can be converted to 1-chloro-F-butane by aerosol direct fluorination in isolated yields, approaching 38%. The product distribution of F-n-butyl chloride was 60.2% by glc assay.

t-Butyl Chloride- 2-Methyl-2-chloropropane can be converted to F-tert-butyl chloride by aerosol direct fluorination in yields approaching 43%. The

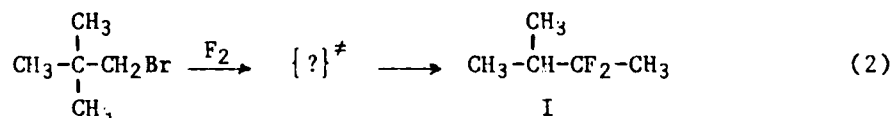
product distribution of F-t-butyl chloride was 80.4% of all products collected.

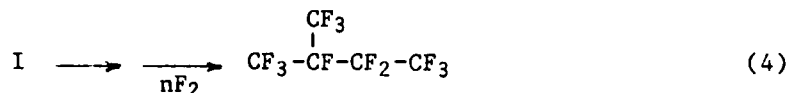
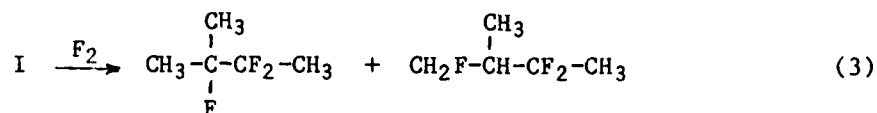
Cyclopentane-As a preliminary experiment to the fluorination of two chlorinated cyclopentanes, cyclopentane was fluorinated at a 2.0 mmole/hr throughput with photochemical finishing. The product was fractionated through -63° , -131°C and -196°C traps. The -131°C trap consisted of 80% to 90% perfluorocyclopentane. The glc isolated yield was 29% based on the calculated throughput.

Chlorocyclopentane- Chlorocyclopentane was fluorinated with photochemical finishing at throughputs of from 1 to 2.4 millimoles per hour. The assay of the product collected consisted of C_4F_{10} (2.5%), cy- C_5F_{10} (12.5%) $\text{C}_5\text{ClF}_{11}$ (12.5% and 15.5% two products), and cy- C_5ClF_9 (50%). Chlorocyclopentane was the major product in all reactions. The yield of chloro-F-cyclopentane based on theoretical throughput is 42%.

Dichlorocyclopentane- Aerosol fluorination of trans-1,2-dichlorocyclopentane prepared by the method of Gousseron et. al.¹⁵ was fluorinated at a 1 millimole/hr, throughput with photochemical finishing. The major product (38% yield) collected consisted of F-1,2-dichlorocyclopentane with a 75:25 mix of trans:cis isomers. Other products isolated [percent yields] were: cy- $\text{C}_5\text{F}_9\text{Cl}$ [24%], $\text{C}_5\text{F}_{10}\text{Cl}_2$ [4%], $\text{C}_5\text{F}_{11}\text{Cl}$ [1.3%], cy- C_5F_{10} [6%]. Percent of theoretical yields were in this case the same as the distribution, i.e. 100% product recovery. It is apparent from the proceeding experiments that retention of a chlorine substituent is not difficult. A much more vexing problem is the retention of bromine substituents. Iodine substituents were not tried due to their known reactivity with fluorine. The only alkyl bromide tried to date has been neopentyl bromide.

Neopentyl Bromide: Bromoneopentane was prepared by the bromination of neopentyl alcohol according to the method of Wiley, *et. al.*¹³ Aerosol direct fluorination of bromoneopentane was initially directed at perfluorination. A 2 millimole per hour throughput of bromoneopentane was fluorinated with photochemical finishing to yield product consisting of 40% F-isopentane, 15% each F-isobutane and 2-methyl-3,3-difluorobutane, 8% 2-fluoro-2-methyl-3,3-difluorobutane, elemental bromine and lesser products. The most significant finding of this experiment is the rearrangement of the neopentyl group. A more perplexing problem is the "abnormal" secondary product isomer distribution. The facility with which neopentyl cations rearrange to isopentyl cations is a well known phenomenon. The tendency of neopentyl radical and anions to rearrange is not very pronounced. The almost complete rearrangement of the neopentyl moiety almost certainly implies an ionic or polar mechanism. Since this rearrangement on fluorination does not occur for the chloroneopentane, the causative factor must be due to fluorine attack on bromine resulting in a cationic or polar intermediate. Since fluorocarbons do not readily undergo alkyl shifts the rearrangement must occur at a very early stage in the reaction. To test this hypothesis and to serve as a control the above reaction was repeated but without photochemical finishing. The major products isolated were 2-methyl-3,3-difluorobutane (20%), 1-fluoro-2-methyl-3,3-difluorobutane (20%), 2-fluoro-2-methyl-3,3-difluorobutane (10%). The remaining products were mixtures of isopentanes having 4,5 and 6 fluorine substituents. The sequence of events in both fluorination experiments seems to be best explained by the following reaction sequence,





The nature of the intermediate[‡] in equation (2) is unknown but undoubtedly it is highly polar and likely contributes to the fluorination of the methylene group bearing the bromine. It is tempting to speculate on mechanisms to explain the "abnormal" products whose prototype is compound (I). It seems reasonable to assume that an alkyl bromine fluoride; R-BrF_n, n=2,4; analog of BrF₃ or BrF₅ might be involved. This seems an excellent problem for matrix isolation esr and infrared using a fluorine or fluorine inert gas matrix.

AEROSOL DIRECT FLUORINATION OF VARIOUS CARBONYL FUNCTIONAL GROUPS

Acyl (Acid) Halides: The LTG fluorination of acyl halides is limited to the acyl fluorides because of the tendency of the molecules to decarbonylate on formation of the acyl radical intermediate when fluorine replaces the acyl halogen (e.g. Cl, Br). The LTG fluorination of pivaloyl fluoride, however, gave good yields of its perfluoro analog.¹⁶ Because of acidity differences between LTG and Aerosol fluorinations (discussed elsewhere) we felt that acid chlorides might be fluorinated intact. This assumption proved correct pivaloyl chloride can be converted to F-pivaloyl fluoride in yields approaching 60% with very little decarbonylization.

Ketones: Most direct fluorination and other fluorination processes have failed miserably to perfluorinate ketones although several reports of their syntheses occur in the literature.¹⁷ We attempted this functional group with pessimism because of the known catalysis of F-ketones by fluoride ion to give fluoroxy compounds. Attempts to fluorinate acetone were not successful. Our major products had only one or two fluorines or none at all even when large excesses of fluorine and higher aerosol generator temperatures were used. We have concluded from various evidence that acetone partially dissolves sodium fluoride and results in large agglomerated droplets of solution (instead of a finely divided aerosol) which adhere to the walls of the reactor and are released only at the higher temperatures following conclusion of the reaction. Double product traps proved this to be the case. If the polarity (dielectric constant) of acetone is too high (i.e. dissolves sodium fluoride), a better ketone to fluorinate would have longer alkyl groups. Our next candidate was 3-pentanone.

The aerosol direct fluorination of 3-pentanone, diethyl ketone, proved quite successful. A photochemically finished aerosol fluorination of

3-pentanone produced raw product containing 60% F-3-pentanone as characterized by IR, mass spectra and ^{19}F NMR (Table 4). This extraordinary success surprised and pleased us and has been repeated several times. The next ketone attempted successfully was di-n-propyl ketone. The photochemically finished aerosol fluorination of 4-heptanone produced raw product containing 92% F-4-heptanone as characterized by IR, mass spectra and ^{19}F NMR (Tables 4).

Having been spurred by the above successes with acyclic ketones we attempted the aerosol direct fluorination of cyclic ketones. Cyclic F-ketones are not readily available by condensation procedures.^{18,19} The photochemically finished aerosol fluorination of cyclopentanone produced raw product containing 61% F-pentanoyl fluoride and 18% F-butane (Table 5). No traces of F-cyclopentanone were isolated. Apparently ring opening with some decarbonylation are the only significant results. Because cyclopentanone is subject to some bond angle strain at the carbonyl carbon-carbon bonds it may be possible to obtain other cyclic ketones by aerosol direct fluorination. We are currently planning to fluorinate cycloheptanone to try and correlate our results to structure.

Esters: The major failure of the Aerosol process vis-a-vis the LTG process is the direct fluorination of ethyl acetate.¹⁶ LTG direct fluorination of ethyl acetate is tricky however, requiring cooling of the NaF-hydrogen fluoride scrubbers to prevent cleavage of the perfluoroester to two acid fluoride fragments.²⁰ The high concentration of fluoride ion in the Aerosol reaction, and its highly active form, makes us very pessimistic about the applicability of aerosol fluorination to species which undergo undesirable side reactions catalysed by fluoride ion.

TABLE 4

CHARACTERIZATION OF F-KETONES
Infrared and Mass Spectra

F-3-Pentanone:

Infrared (cm^{-1}): 3620(w), 1780(m), 1320(s), 1230(vs), 1175(vs), 1110(s), 1025(m), 880(m), 830(m), 750(m), 710(s), 600(m).

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

CI (CH_4): 267(100) $\text{C}_5\text{F}_{10}\text{OH}, \text{M}+\text{H}$; 247(31) $\text{C}_5\text{F}_9\text{O}$, (M-F); 147(31) $\text{C}_3\text{F}_5\text{O}$; 119(14) C_2F_5 ; 69(4) CF_3 .

EI(70eV): 148(1) $^{13}\text{CC}_2\text{F}_5\text{O}$; 147(40) $\text{C}_3\text{F}_5\text{O}$; 131(1) C_3F_5 ; 128(1) $\text{C}_3\text{F}_4\text{O}$; 119(100) C_2F_5 ; 109(1) $\text{C}_3\text{F}_3\text{O}$; 101(1) $^{13}\text{CCF}_4$; 100(12) C_2F_4 ; 98(1) C_3F_3 ; 81(1) C_2F_3 ; 78(1) $\text{C}_2\text{F}_2\text{O}$; 69(32) CF_3 ; 50(2) CF_2 ; 31(3) CF .

^{19}F NMR $\phi_{\text{CFCI}_3} = 0.0$ ppm:

$\phi_{\text{CF}_3} = -82.03$ ppm(s)

$J < 1$ hz, Integration 3:2

$\phi_{\text{CF}_2} = -121.38$ ppm(s)

F-4-Heptanone:

Infrared (cm^{-1}): 1785(m), 1395(m), 1240(s), 1200(m); 1160(m), 1140(m), 1080(m), 1015(m), 845(m), 780(w), 945(m), 925(m), 900(m).

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

CI(CH_4): 367(39) $\text{C}_7\text{F}_{14}\text{OH}$, M+H; 347(100) $\text{C}_7\text{F}_{13}\text{O}$, M-F.

EI(70eV): 347(7) $\text{C}_7\text{F}_{13}\text{O}$, M-F; 197(15) $\text{C}_4\text{F}_7\text{O}$; 169(100) C_3F_7 ; 119(15) C_2F_5 ; 100(16) C_2F_4 ; 69(81) CF_3 .

^{19}F NMR $\phi_{\text{CFCI}_3} = 0.0$ ppm:

	Integral
$\phi_{\text{CF}_3} = -81.16$ ppm (m)	3
$\phi_{\text{CF}_2} = -126.31$ ppm (m)	2
$\phi_{\text{CF}_2} = -118.66$ ppm (m)	2

TABLE 5

CHARACTERIZATION OF F-PENTANOYL FLUORIDE

Infrared (cm^{-1}): 1880(s), 1350(w), 1275(m), 1265(s), 1240(vs), 1215(s), 1140(s), 1110(s), 1020(s), 945(m), 930(m), 905(m), 875(m), 840(w), 825(w), 815(m), 740(m), 710(m).

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

CI (CH_4): 418 (10.7) $\text{C}_{10}\text{F}_{14}\text{O}_2$; 281 (10.7) $\text{C}_5\text{F}_9\text{O}_3\text{H}_2$; 266 (0.7) $\text{C}_5\text{F}_{10}\text{O}$, M; 247 (6.5) $\text{C}_5\text{F}_9\text{O}$, M-F; 220 (4.3) $^{13}\text{CC}_3\text{F}_9$, 219 (100) C_4F_9 , M-CFO; 197 (7.2) $\text{C}_4\text{F}_7\text{O}$, M- CF_3 ; 131 (12.5) C_3F_5 ; 103 (5.7) ???; 101 (9.2) $\text{C}_2\text{F}_4\text{H}$; 100 (3.8) C_2F_4 ; 69 (2.7) CF_3 .

EI (70eV): 219 (3.8) C_4F_9 ; 169 (19) C_3F_7 ; 131 (16.7) C_3F_5 ; 119 (21.6) C_2F_5 ; 100 (10) C_2F_4 ; 78 (5.7) $\text{C}_2\text{F}_2\text{O}$; 69 (100) CF_3 ; 47 (7.3) CFO.

^{19}F NMR $\phi_{\text{CFCl}_3} \equiv 0.0$ ppm $\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-C}^{\text{O}}_{\text{F}_e}$
 $\begin{matrix} & & & & & \text{O} \\ & & & & & \text{F}_e \\ & & & & & \\ \text{a} & \text{b} & \text{c} & \text{d} & & \end{matrix}$

(Mult.) [Integ.]

 $\phi_a = -81.59$ ppm (t•t) [3] $J_{ac} = 9.76$ hz $J_{ab} = 2.14$ hz (cont 2.44/1.83 hz) $\phi_b = -126.47$ ppm (m) [2] $J_{bc} = 3.05$ hz $\phi_c = -123.98$ ppm (m) [2] $J_{bd} = 9.76$ hz $J_{ad} = 1.83$ hz $\phi_d = -118.32$ ppm (~q•q) [2] $J_{ce}+J_{de} = 7.33$ hz $\phi_e = +24.85$ ppm (p) [1]

AEROSOL FLUORINATION OF VARIOUS FUNCTIONAL GROUPS

Alkyl Sulfides: The weakness of the carbon-sulfur bond (~ 180 KJ/mole) and the tendency of sulfur to undergo oxidation preclude the possibility of producing perfluoroalkyl sulfides.²¹ Previous attempts to fluorinate dimethylsulfide resulted in only CF_3SF_5 .²¹ Although aerosol fluorination was able to retain both carbon-sulfur bonds producing trans-bis(trifluoromethyl)-sulfur tetrafluoride, $(\text{CF}_3)_2\text{SF}_4$, yields were low (5-10%) and CF_3SF_5 predominated (30%). In all reactions oil was found in the initial stages and many partially fluorinated and hygroscopic products were formed.

Amines: Amines have remained troublesome for direct fluorination. The lability of the very stable $(\text{R}_\text{F})_2\text{N}$ radical ($\text{R}_\text{F}=\text{F}$, CF_3 , etc.) virtually assures carbon-nitrogen bond cleavage, and loss of the bulkiest alkyl group. Aerosol fluorination of tert-butyl amine in all attempts produces excellent yields of F-isobutane. If the fluorine concentration is reduced or the photochemical stage not activated the result is less fluorinated isobutanes. Apparently one of the first reactions to occur is the fluorination of the amine grouping and its loss as NF_2/NF_3 .

Aerosol fluorination of morpholine was carried out under varied condition of carrier flow, throughput and fluorine stoichiometry. Morpholine invariably produces excellent yields of perfluoroethylether and relatively low yields of perfluoro-N-fluoromorpholine. This compound had a tendency to produce tar in the reactor and significant quantities of partially fluorinated compounds when the fluorine concentration was low.

The success of Simons electrochemical process in producing perfluoro-tertiary amines must be in part due to the highly acidic HF solvent which undoubtedly protonates the amine. If this is the case the use of BF_3 -amine

adducts may well allow the production of tertiary amines by aerosol fluorination. The production of primary and secondary perfluoroamines is problematical because even the electrochemical process does not work well for these compounds.

OPTIMIZATION OF AEROSOL FLUORINATIONS-YIELDS VERSUS PRODUCT DISTRIBUTIONS

Optimization of reaction parameters in aerosol direct fluorinations is emerging from the realm of "magic" to one of art verging on science. The most critical component in the aerosol fluorinator is the aerosol generator. Whether a reactant forms a highly dispersed crystalline aerosol or something less ideal can critically affect the performance of the fluorination. The excellent yields of F-neopentane are in part due to the almost invariably good aerosol dispersions they give. Materials which form liquid phase aerosols or supercool badly tend to stick to interior surfaces in the aerosol reactor (cf acetone).

Perhaps the most important variable affecting the condition of the hydrocarbon aerosol is the carrier flow laden with the nucleating preaerosol. If this flow is too low for the particular hydrocarbon and throughput, the aerosol fluorination is adversely affected. For example in Table 6 (p 38) the "percent reaction" of reaction numbers 8 (main carrier 400 mL/m) and 11 (main carrier 800 mL/m) are 32% and 87%. The percent unfluorinated 2,4-dimethylpentane to monofluoro to difluoro ratios for the two reactions are 68:24:7 and 13:25:32 respectively (Table 2). The major effect of carrier increase is to decrease the amount of unfluorinated 2,4-dimethylpentane. Since both reaction time and fluorine concentration decrease in these two runs the reason for the greater extent of reaction must be a more efficient generation of a finer more reactive hydrocarbon aerosol. This effect definitely is a result of optimization because increase of the main carrier to 2300 mL/min. in reaction 14 drops the "percent reaction" to 65% and the product ratio to 35:85:18 for zero, one and two fluorines; a definite dilution effect is operating here.

The above relationships caused us to reexamine some of our prior reactions where yields were low. A double trap system was employed. The product collecting during the reaction went into the second trap (-196°C) in the series. When the hydrocarbon throughput was shut off, the first trap was cooled to -196°C during the time (usually overnight) required for the reactor to reach ambient temperature while passing a low (<100 mL/min) total flow of helium from all inlets. In almost every case the product distribution of perfluorinated species was 60% to 92% of the lot in the second trap with less than 5% passing the -131°C vacuum line fractionation and collecting in the -196°C trap. The first trap usually contained very poorly fluorinated or unfluorinated hydrocarbons in variable amounts. This of course was especially the case in the attempt to fluorinate acetone. In that reaction no products collected during the reaction and primarily only acetone was collected in the first trap, which was cooled at the close of the reaction.

The next obvious step was to begin conducting photochemically finished reactions at the higher flow rates. The only reason main carrier flows had been minimized initially was to maximize the fluorine concentration. The concentration of fluorine is important for "dark" reactions seeking higher percent fluorination levels up to but not including perfluorination which is most easily achieved by photochemical finishing. For reactions up to about 40% fluorination the stoichiometry not the concentration is more important.*

The results of these main carrier increases for photochemically finished reactions having at most five percent fluorine reactant concentration are shown in Table 9. For example, actual yields of F-neopentyl chloride rose from 13% to 74%; F-n-butyl chloride rose from 15% to 38%; F-tert-butyl

*See for example reactions 8 and 9 and reactions 12 and 13 in Table 2 and discussion on p 39 of the experimental part.

chloride rose from 20% to 43%; chloro-F-cyclopentane and trans-1,2-dichloro-F-cyclopentane rose to 42% and 38% respectively from less than 10%. Thus our yields are beginning to match product distributions indicating that losses are physical losses not losses due to fragmentation. These results are quite significant and indicate that despite our advances we have only begun to understand the potential of this new fluorination technique.

EXPERIMENTAL

The basic aerosol fluorinator design and a basic description of the process is presented elsewhere.^{1,22} 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 (CH₄ plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980 A MS, 5934A Computer); and ¹H and ¹⁹F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in CDCl₃ with 1% CFC1₃ internal standard. Elemental Analyses where necessary are performed by Schwartzkopf Microanalytical Laboratories, Woodside, N.Y.

Aerosol Fluorination of 2,4-Dimethylpentane: 2,4-Dimethylpentane was purchased from Aldrich Chemical Co. and was used as received. Throughput determinations were determined gas chromatographically based on the following vapor pressure curve (T°C, Pvp. mm Hg): 22°,85; -22°,8; -25°,6; -30°,4; -46°,2; -78°,1. Maintenance of the hydrocarbon reservoir at -22°C and sparged with a flow of 75 mL/min of helium produced the desired throughput of 2.0 millimole/hour of 2,4-dimethylpentane. Details of fluorination conditions are contained in Table 6. Omitted reaction numbers are for experiments which produced excessive fluorination or otherwise failed. Products

TABLE 6
AEROSOL FLUORINATION OF 2,4-DIMETHYLPENTANE

Run No.	Fluorine Flow ml/min		Helium Diluent ml/min. Reactor		Reaction Temp °C		Main Helium ml/m Carrier	Overall Stoichiometry he:F ₂	Percent F ₂ concl.	Reactor Volume ml length	Reaction Time-sec	Percent Reaction
	Mod 1	Mod 2	Reactor	Mod 1	Mod 2	Reactor						
4	0.6	-	7	-	-	-55	-30	0	0.12	1431	178	51%
5	0.65	-	10	-	-	-60	-30	5	0.073	1431	97	75%
8	-	0.8	-	30	-	-60	-30	10	0.16	288	34	32%
9	-	1.1	-	30	-	-55	-40	0	0.22	288	34	55%
10	-	1.1	-	30	-	-55	-35	0	0.12	288	19	94%
11	-	0.8	-	30	-	-55	-40	0	0.088	288	19	87%
12	-	0.4	-	30	-	-60	-30	0	0.030	288	13	18%
13	-	0.4	-	30	-	-55	-40	0	0.017	288	7.2	19%
14	-	0.8	-	30	-	-55	-30	0	0.033	288	7.2	65%
15	0.6	-	40	-	-	-60	-30	10	0.066	1355	89	37%
16	-	0.8	-	40	-	-55	-30	0	0.087	1355	89	41%
17	-	0.8	-	35	-	-55	-30	0	0.088	1355	89	22%
18	-	0.8	-	35	-	-50	-30	10	0.088	1355	89	32%
19	-	1.2	-	35	-	-55	-30	0	0.13	1355	89	26%
20	-	1.5	-	20	-	-55	-30	0	0.17	1355	91	27%

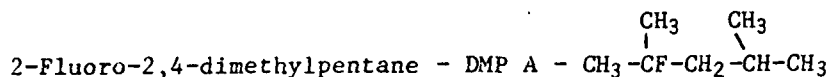
separated by gas chromatography are listed in Tables 1 and 2. Characterization of each of the species are given in Tables 7 and 8.

Each reaction in Table 6 represents an attempt to maximize monofluorination by alteration of the reaction parameters. The most important parameter is the amount of fluorine and not its concentration (cf reactions 8 and 9, 12 and 13). All the parameters interact in a complicated way and many responses are not linear throughout their controllable range (cf rxns. 8,11,14). In the former case, reactions 8 and 9 the amount of F_2 is increased 38% the amount of reaction doubles, the amount of monofluoro is increased by 50% the amount of difluoro almost triples (see Table 2). But in reactions 12 and 13 the amount of fluorine remains constant, the reaction time and the fluorine concentration are halved (carrier flow doubled) but the amount of reaction is almost constant as are the amounts of monofluoro and difluoro-2,4-dimethylpentane. In contrast in reactions 8,11,14 the amount of fluorine is constant, the fluorine concentration and the reaction time decrease as a function of carrier flow through the constant active reactor volume but the percent reaction first increases from 32% to 87% then decreases to 65%. The degree of monofluorination is relatively constant but difluorination follows the percent reaction pattern (e.g. 7%:32%:18%). The response to carrier flows of 400 mL/m; 800 mL/m. and 2300 mL/m are not linear. It seems clear that carrier flows of less than 800 mL/min are out of the linear response range. Furthermore it seems obvious that the reaction between F_2 and alkane is very fast at the mono and difluorination level.

Neopentane/Boron Trifluoride Reactions: Neopentane (2 millimoles/hr) was admitted into a dual inlet aerosol generator opposite a 3 cc/min boron trifluoride flow (8 millimoles/hr) perpendicular to the helium carrier flow

TABLE 7

CHARACTERIZATION OF 2,4-DIMETHYLPENTANES
Infrared and Mass Spectra

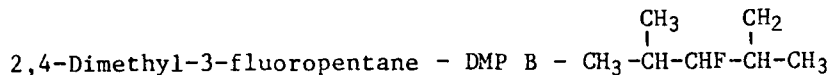


Infrared (cm^{-1}): 2970(vs); 2940(s); 2880(s); 1470(m); 1390(m); 1305(w);
1215(vw); 1110(w); 1065(w); 940(vw); 830(w); 730(vw)

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

CI (CH_4): 99 (13) C_7H_{15} ; 98 (34) C_7H_{14} ; 97 (65) C_7H_{13} ; 3 (100)
 C_6H_{11} , 71 (14) C_5H_{11} .

EI (70eV): 99 (2.7) C_7H_{15} ; 98 (39.6) C_7H_{14} ; 83 (100) C_6H_{11} ; 55
(57) C_4H_7 ; 41 (18) C_3H_5 .

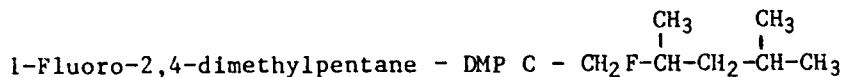


Infrared (cm^{-1}): 2975(vs); 2950(sh,s); 2925(sh,.s); 2890(s); 1480(m);
1395(m); 1105(w); 1005(sh,m); 980(s); 910(w); 800(w).

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

CI (CH_4): 119 (1.2) $\text{C}_7\text{H}_{16}\text{F}$, M+H; 117 (2.4) $\text{C}_7\text{H}_{15}\text{F}$; 99 (79) C_7H_{15} .
M-F; 98 (44) C_7H_{14} ; 97 (100) C_7H_{13} ; 83 (66) C_6H_{11} ; 71
(13) $\text{C}_4\text{H}_4\text{F}$.

EI (70eV): 119 (5.1) $\text{C}_7\text{H}_{16}\text{F}$; 118 (1.1) $\text{C}_7\text{H}_{15}\text{F}$; 98 (55) C_7H_{14} ; 83
(100) C_6H_{11} ; 56 (19) C_4H_8 ; 55 (47) C_4H_7 ; 43 (11) C_3H_7 ;
41 (16) C_3H_5 .



Infrared (cm^{-1}): 2965(vs); 2910(sh,s); 2860(sh,w); 1480(m); 1395(m);
1295(w); 1250(m); 1230(sh,w); 1175(w); 1080(w); 1040(s)
985(w); 830(vw); 750(vw).

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

CI (CH_4): 119 (4.5) $\text{C}_7\text{H}_{16}\text{F}$, M+H; 117 (22) $\text{C}_7\text{H}_{14}\text{F}$; 99 (77) C_7H_{15} ;
98 (15) C_7H_{14} ; 97 (100) C_7H_{13} ; 85 (10) C_6H_{13} ; 83 (53)
 C_6H_{11} ; 77 (16) C_6H_5 ; 75 (23) $\text{C}_4\text{H}_8\text{F}$; 69 (30) C_5H_9 ; 61
(42) $\text{C}_3\text{H}_6\text{F}$; 59 (50) $\text{C}_3\text{H}_4\text{F}$.

TABLE 7 (CONTINUED)

EI (70eV): 119 (4.4) C₇H₁₆F; 85 (23) C₆H₁₃; 83 (25) C₆H₁₁; 74 (13) C₄H₇F; 69 (27) C₅H₉; 61 (25) C₃H₆F; 57 (39) C₄H₉; 56 (43) C₄H₈; 55 (39) C₄H₇; 43 (100) C₃H₇; 42 (57) C₃H₆; 41 (50) C₃H₅; 39 (15) C₃H₃.

1,1-Difluoro-2,4-dimethylpentane - DMP D₁ - $\text{CHF}_2\text{-}\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{-CH}_2\text{-}\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{-CH}_3$

Infrared (cm⁻¹):

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

CI (CH₄): 136 (1) C₇H₁₄F₂, M; 135 (19) C₇H₁₃F₂; 115 (19) C₇H₁₂F; 99 (11) C₇H₁₅; 97 (27) C₇H₁₃; 95 (39) C₇H₁₁; 77 (14) C₃H₃F₂; 75 (16) C₄H₈F; 73 (43) C₄H₆F; 61 (96) C₃H₆F; 59 (100) C₃H₄F.

EI (70eV): 131 (16) C₇H₉F₂; 119 (14) C₇H₁₆F; 103 (25) C₆H₁₂F; 99 (11) C₇H₁₅; 92 (16) C₄H₆F₂; 83 (46) C₆H₁₁; 79 (14) C₃H₅F₂; 77 (26) C₃H₃F₂; 74 (18) C₄H₇F; 73 (31) C₄H₆F; 69 (16) C₅H₉; 65 (16) C₂H₃F₂; 61 (63) C₃H₆F; 59 (21) C₃H₄F; 57 (12) C₄H₉; 56 (13) C₄H₈; 55 (24) C₄H₇; 51 (27) CHF₂; 47 (18) C₂H₄F; 44 (23) C₂HF; 43 (100) C₃H₇; 42 (21) C₃H₆; 41 (44) C₃H₅; 39 (20) C₃H₃.

1,4-Difluoro-2,4-dimethylpentane - DMP D₂ - $\text{CH}_2\text{F-}\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{-CH}_2\text{-}\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{-CF-CH}_3$

Infrared (cm⁻¹):

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

CI (CH₄): 135 (0.6) C₇H₁₃F₂; 117 (5.5) C₇H₁₄F, M-F; 97 (95) C₇H₁₃; 89 (14) C₅H₁₀F; 61 (100) C₃H₆F; 59 (38) C₃H₄F.

EI (70eV): 134 (1.4) C₇H₁₂F₂; 74 (33) C₄H₇F; 61 (100) C₃H₆F; 44 (10) C₂HF; 43 (19) C₃H₇; 41 (23) C₃H₅.

1-2-Difluoro-2,4-Dimethylpentane-(RS) - DMP E - $\text{CH}_2\text{F-}\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{-CF-CH}_2\text{-}\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{-CH}_3$

Infrared (cm⁻¹): 2990 (sh,s); 2970(vs); 2945(sh,s); 2890(m); 1470(m); 1375(bd,m); 1300(w); 1260(w); 1165(dblt.,w); 1130(m); 1070(sh,s); 1055 (vs); 1015(w); 990(dblt., w); 905(m); 855(w); 770(w).

TABLE 7 (CONTINUED)

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

CI (CH₄): 135 (3.4) C₇H₁₃F₂; 119 (12) C₇H₁₆F; 117 (28) C₇H₁₄F, M-F; 115 (14) C₇H₁₂F; 97 (100) C₇H₁₃, M-HF₂; 95 (31) C₇H₁₁; 83 (12) C₆H₁₁; 75 (43) C₄H₈F; 73 (25) C₄H₆F; 61 (51) C₃H₁₆F.

EI (70eV): 131 (3.3) C₇H₉F₂; 119 (3.9) C₇H₁₆F; 117 (1.7) C₇H₁₄F; 103 (24) C₆H₁₂F; 83 (36) C₆H₁₁; 79 (20) C₆H₇, C₃H₅F₂; 75 (14) C₄H₈F; 74 (41) C₄H₇F; 73 (19) C₄H₆F; 69 (13) C₅H₉; 61 (50) C₃H₆F; 60 (12) C₃H₅F; 59 (21) C₃H₄F; 56 (18) C₄H₈; 55 (24) C₄H₇; 51 (11) C₄H₃; 47 (11) C₂H₄F; 43 (100) C₃H₇; 42 (22) C₃H₆; 41 (32) C₃H₅.

1,3-Difluoro-2,4-dimethylpentane-RR;SS;RS;SR - DMP F - $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_2\text{F}-\text{CH}-\text{CHF}-\text{CH}-\text{CH}_3 \end{array}$

Infrared (cm⁻¹): 2975(vs); 2940(sh,m); 2915(sh,m); 2895(m); 1480(m); 1395(m); 1100(w); 1080(w); 1035(s); 985(m); 910(w).

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

CI (CH₄): 135 (0.6) C₇H₁₃F₂; 117 (32) C₇H₁₄F; 97 (100) C₇H₁₃, M-HF₂; 75 (11) C₄H₈F.

EI (70eV): 119 (24) C₇H₁₆F; 75 (26) C₄H₈F; 74 (30) C₄H₇F; 73 (13) C₄H₆F; 69 (19) C₅H₉; 61 (12) C₃H₆F; 59 (19) C₃H₄F; 55 (23) C₄H₇; 47 (20) C₂H₄F; 44 (22) C₂HF; 43 (100) C₃H₇; 42 (80) C₃H₆; 41 (34) C₃H₅.

1-Fluoro-2-fluoromethyl-4-methylpentane - DMP G - $\begin{array}{c} \text{CH}_2\text{F} \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_2\text{F}-\text{CH}-\text{CH}_2\text{CH}-\text{CH}_3 \end{array}$

Infrared (cm⁻¹): 2910(vs); 2940(s); 2915(s); 2885(m); 1480(m); 1395(m); 1295(w); 1250(w); 1195(w); 1150(sh,m); 1120(m); 1035(s); 980(w); 905(w); 810(vw).

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

CI (CH₄): 135 (2.2) C₇H₁₃F₂ (M-H); 117 (11) C₇H₁₄F, M-F; 97 (100) C₇H₁₃; 95 (19) C₇H₁₁; 75 (52) C₄H₈F; 69 (15) C₅H₉; 61 (42) C₃H₆F; 59 (13) C₃H₄F.

TABLE 7 (CONTINUED)

EI (70eV):

Unidentified Difluoro-2,4-dimethylpentane - DMP G1 -Infrared (cm^{-1}):

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

CI (CH_4): 121 (5.2) $\text{C}_6\text{H}_{11}\text{F}_2$, M- CH_3 ; 119 (32) $\text{C}_7\text{H}_{16}\text{F}$; 117 (50) $\text{C}_7\text{H}_{14}\text{F}$, M-F; 97 (55) C_7H_{13} ; 95 (16) C_7H_{11} ; 77 (22) $\text{C}_3\text{H}_3\text{F}_2$; 75 (100) $\text{C}_4\text{H}_8\text{F}$; 73 (44) $\text{C}_4\text{H}_6\text{F}$; 71 (31) $\text{C}_4\text{H}_4\text{F}$; 61 (66) $\text{C}_3\text{H}_6\text{F}$; 59 (59) $\text{C}_3\text{H}_5\text{F}$.

EI (70eV): 131 (6.4) $\text{C}_7\text{H}_9\text{F}_2$; 119 (8.0) $\text{C}_7\text{H}_{16}\text{F}$; 117 (6.7) $\text{C}_7\text{H}_{14}\text{F}$, M-F; 77 (11) $\text{C}_3\text{H}_3\text{F}_2$; 74 (11) $\text{C}_7\text{H}_7\text{F}$; 73 (12) $\text{C}_4\text{H}_6\text{F}$; 71 (14) $\text{C}_4\text{H}_4\text{F}$; 69 (12) C_5H_9 ; 61 (53) $\text{C}_3\text{H}_6\text{F}$; 60 (12) $\text{C}_3\text{H}_5\text{F}$; 59 (18) $\text{C}_3\text{H}_4\text{F}$; 55 (11) C_4H_7 ; 47 (15) $\text{C}_2\text{H}_4\text{F}$; 43 (100) C_3H_7 ; 42 (19) C_3H_6 ; 41 (29) C_3H_5 ; 32 (85) CHF.

$\begin{array}{cc} \text{CH}_3 & \text{CH}_3 \\ | & | \end{array}$
1,5-Difluoro-2,4-dimethylpentane - (RS+meso) - DMP H - $\text{CH}_2\text{F}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2\text{F}$

Infrared (cm^{-1}): 2965(vs); 2900(s); 14 0(m); 1400(m); 1230(w); 1200(w); 1120(sh,m); 1103(m); 1075(m); 1035(vs); 990(m); 950(sh,w); 915(sh,m); 910(vw).

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

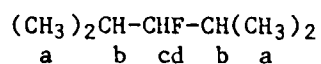
CI (CH_4): 135 (2.1) $\text{C}_7\text{H}_{13}\text{F}_2$, M-H; 97 (100) C_7H_{13} ; 75 (32) $\text{C}_4\text{H}_8\text{F}$; 61 (23) $\text{C}_3\text{H}_6\text{F}$; 59 (14) $\text{C}_3\text{H}_4\text{F}$.

EI (70eV):

TABLE 8

CHARACTERIZATION OF 2,4-DIMETHYLPENTANES
Nuclear Magnetic Resonance

2,4-Dimethyl-3-fluoropentane (DMP B)

 $\frac{^{19}\text{F}}$

$$\phi_d = \quad \text{ppm} \quad J_{cd} = \quad \text{hz}$$

 $\frac{^1\text{H}}$

$$\delta_a = 0.95 \text{ ppm}$$

$$J_{ab} = 7 \text{ hz}$$

$$J_{ad} = 1 \text{ hz}$$

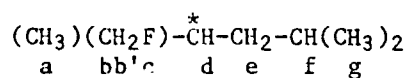
$$\delta_b = 1.5-2.3 \text{ ppm}$$

(complex multiplet)

$$\delta_c = 3.8 \text{ ppm (d.t)}$$

$$J_{cd} = 49 \text{ hz}$$

R.S.-1-Fluoro-2,4-dimethylpentane (DMPC)

 $\frac{^{19}\text{F}}$

$$\phi_c = -222.7 \text{ (t.d)}$$

$$J_{bc} = 47.6 \text{ hz (t)}$$

$$J_{cd} = 18.9 \text{ hz (d)}$$

$$\delta_a, \delta_g = 0.86 \text{ ppm (m)}$$

$$\delta_e = 1.1 \text{ ppm (t)}$$

$$\delta_d, \delta_f = 1.6 \text{ ppm (m)}$$

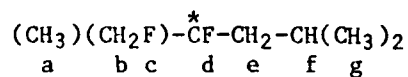
$$\delta_b = 4.1 \text{ ppm (d.d.d)}$$

$$J_{b'c}, J_{bc} = 47.6 \text{ hz}$$

$$J_{bd} = 6.11 \text{ hz}$$

$$J_{b'd} = 5.61 \text{ hz}$$

1,2-Difluoro-2,4-dimethylpentane (DMP E)

 $\frac{^{19}\text{F}}$

$$\phi_c = -228.8 \text{ ppm (t.d)}$$

$$\phi_d = -154. \text{ ppm (t)}$$

$$J_{bc} = 48.8 \text{ hz}$$

$$J_{cd} = 12.2 \text{ hz}$$

$$J_{bd} = 18.3 \text{ hz}$$

$$\delta_a = 1.37 \text{ ppm (d.d)}$$

$$J_{ac} = 21.24 \text{ hz}$$

$$J_{ad} = 1.95 \text{ hz}$$

$$\delta_g = 0.96 \text{ ppm (d)}$$

$$J_{fg} = 6.7 \text{ hz}$$

$$\delta_e, \delta_f = 1.5-1.8 \text{ ppm (m)}$$

$$\delta_b = 4.40 \text{ ppm (d.d)}$$

$$J_{bc} = 47.7 \text{ hz}$$

$$J_{bd} = 18.2 \text{ hz}$$

* = asymmetric carbons

TABLE 8 (CONTINUED)

(RR,SS;RS,SR)-1,3-Difluoro-2,4-dimethylpentane ^a (DMP-F)		¹ H
(CH ₃) (CH ₂ F)- [*] CH- [*] CHF-CH(CH ₃) ₂		δ _a , δ _h = 0.96 ppm (d.d.d)
a	b c d ef g h	J _{ab} , J _{gh} = 6.84 hz
Mixture of two diastereoisomers: RR,SS and RS,SR		δ _d , δ _g = 1.5-2.4 ppm (m)
		δ _b , δ _e = 4.3 ppm (m)
		J _{ef} , J _{bc} = 47.36, hz

¹⁹ F	¹⁹ F
φ _{c1} = -222.68 ppm (t.d)	φ _{f1} = -199.9 ppm (m)
J _{bc} = 45.58 hz	J _{ef} = 42.72 hz
J _{cd} = 15.3 hz	φ _{f2} = -201.3 ppm (m)
φ _{c2} = -230.48 ppm (t.d)	J _{ef} = 42.7 hz
J _{bc} = 45.7 hz	
J _{cd} = 24 hz	

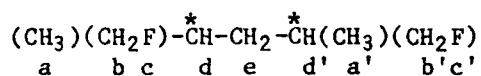
1-fluoro-2-fluoromethyl-4-methylpentane (DMP-G)

(CH ₂ F) ₂ CH-CH ₂ -CH(CH ₃) ₂		
a	b c d e f	
¹⁹ F	¹ H	
φ _b = -229.0 ppm (t.d)	δ _f = 0.91 ppm (d)	
J _{ab} = 47.3 hz	J _{ef} = 6.35 hz	
J _{bc} = 23.3 hz	δ _d = -1.25 (m)	
	δ _e , δ _c = 1.55 ppm (m)	
	δ _a = 4.43 ppm (d.d)	
	J _{ab} = 47.2 hz	
	J _{ac} = 5.23 hz	

*≡asymmetric carbons

TABLE 8 (CONTINUED)

(meso; RS)-2,4-Bis(fluoromethyl)pentane (DMP-H)
(1,5-Difluoro-2,4-dimethylpentane)



$\delta_{a'}, \delta_a = 0.95$ ppm (irr octet)
 $\delta_e = 1.1-1.5$ ppm (ass.m.)

$\delta_d, \delta_{d'} = 1.87$ ppm (nonet)
 $J = 6-7$ hz

$\delta_b, \delta_{b'} = 4.23$ ppm
 $J_{bc} = 47.6$ hz
 $J_{bd} = 5.86$ hz

$\delta_{c1} = -223.57$ ppm (t.d)
 $J_{bc} = 47.3$ hz
 $J_{cd} = 21.3$ hz

$\delta_{c2} = -222.23$ ppm (t.d)
 $J_{bc} = 47.3$ hz
 $J_{cd} = 18.35$ hz

* $\equiv$ assymmetric carbon

containing the sodium fluoride preaerosol.* Fluorine was admitted into the reactor in stoichiometric amounts (24 mmole/hr).

Products exiting the reactor passed through sodium fluoride pellets to remove hydrogen fluoride and the remainder was fractionated through -110°C (CS_2 slush) and -196°C ($\text{N}_2(\text{l})$) cooled traps. Previous investigations showed that ca 90% of the product was trapped at -110°C and the remainder plus exiting BF_3 collected in the -196°C trap was discarded. Fractionation of the -110°C fraction under vacuum through -131°C and -196°C (discarded) traps followed by gas chromatographic separation on the fluorosilicone QF-1 column produced the product distributions shown in Figures 3 and 4 depending on whether photochemical finishing was employed. Characterizations are given elsewhere.²²

Aerosol Fluorination of Neopentyl Chloride: 1-Chloro-2,2-dimethylpropane was prepared by the method of Wiley, et. al. from neopentyl alcohol.¹³ Its vapor pressure at -10°C is such that a flow of 85 cc/min helium through 50 mL of the material contained in a sparge tube evaporator produces a throughput of 0.38 g/hr (3.6 mmole/hr). Details of the aerosol fluorination parameters are given in Table 9. For a 3 hour photochemically finished run, 2.659g of crude product was collected which when vacuum line fractionated [-131 (2.56g), -196 (0.09g discarded)] and gas chromatographically purified on the SE-52 column ($15^{\circ}/5$ min; $10^{\circ}/\text{m}$ to 75° ; $50^{\circ}/\text{m}$ to $150^{\circ}/7$ min) produced 2.03 of F-neopentyl chloride (table 10) 79.6% of the crude material collected, 74% yield based on calculated throughput. Losses (Table 9) on the 400 mL/min carrier runs are due to unreacted material collecting in the reactor and to too large sizes of aerosol particles giving incomplete fluorine exposure to all reactant.

*Lower BF_3 flows were not measurable with our rotometers and significantly higher flows of BF_3 severely retarded the reaction and promoted tar and oil formation.

Aerosol Fluorination of n-Butyl Chloride - 1-Chlorobutane (Eastman, Fisher) was used as received. Its vapor pressure at -10°C is such that a flow of 58 cc/m helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 0.32g/h (3.5 mmol/hr). Details of the aerosol fluorination parameters are given in Table 9. For a 3 hour photochemically finished run, the -131°C vacuum line fraction weighed 1.17g. Separation of product on the SE-52 column ($0^{\circ}\text{C}/5$ min; $10^{\circ}/\text{m}$ to 30° ; $250^{\circ}/\text{m}$ to $180^{\circ}/10$ min) produced 1.01g of F-1-chlorobutane, Table 10, 60% of isolated product, 38% yield based on theoretical throughput. The remaining products were partially fluorinated 1-chlorobutanes.

Aerosol Fluorination of t-Butyl Chloride - 2-Chloro-2-methylpropane (Eastman Fisher) was used as received. Its vapor pressure at -10°C is such that a flow of 13 cc/min helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 0.30g/hour (3.25 millimoles/hr). Details of the aerosol fluorination parameters are given in Table 9. For a 2.0 hour photochemically finished run 0.88g of crude material was collected. Vacuum line fractionation [-131°C (0.844g); -196°C (discarded)] followed by gas chromatographic separation on the SE-52 column produced 0.714g of F-tert-butyl chloride, Table 10, 80.4% of the crude material and 43% yield based on the theoretical throughput.

Aerosol Fluorination of Cyclopentane - Cyclopentane (~50 mL Eastman, Fisher;) contained in a sparge tube evaporator at -44°C through which a helium flow of 100 mL/min was passed, was empirically determined to produce a throughput of 2 millimoles/hr cyclopentane. Details of the aerosol fluorination conditions for a typical photochemically finished reaction are tabulated in Table 9.

TABLE 9

TYPICAL AEROSOL FLUORINATION REACTION PARAMETERS

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 ^a Stoichiometry he:F ₂	Percent F ₂ Conc. Final Stage	Reactor Volume, ml. (α length)	Reaction Time Sec. (α length)	Product Distribution % Collected	Product Yield % Theoretical
	Reactor Mod. 1	Mod. 2	Mod. 1	Reactor Mod. 1	Mod. 2	Reactor Mod. 2	Reactor Mod. 1	Mod. 2								
Neopentyl Chloride	10	9	-	40	40	-	-50°	-30°	400	4.0 (80)	1:12	3.3%	1355	140	52.6%	13.0%
Neopentyl Chloride	20	20	-	80	80	80	-45°	-30°	1000	3.60 (85)	1:41	4.3%	1355	59	79.6%	74.0%
n-Butyl Chloride	10	20	-	30	30	-	-45°	-30°	400	2.0 (32)	1:36	5.8%	1355	156	26%	15%
n-Butyl Chloride	20	20	-	80	80	80	-45°	-30°	1000	3.5 (58)	1:42	4.4%	1355	60	60.2%	38.0%
t-Butyl Chloride	10	20	-	30	30	-	-45°	-30°	400	2.25 (8)	1:36	5.9%	1355	161	34%	20.4%
t-Butyl Chloride	20	20	-	70	70	70	-40°	-30°	1000	3.25 (13)	1:45	4.7%	1355	63	80.4%	43.0%
Cyclopentane	-	40	50	5	5	5	-60°	-30°	400	2 (100)	1:175	21%	1355	123	90%	29%
Chlorocyclopentane	-	40	50	-	9	9	-55°	-50°	400	2.4 (163)	1:146	19%	1355	111	60%	-10%
Chlorocyclopentane	20	20	-	80	80	80	-40°	-30°	1000	2.0 (135)	1:73.2	4%	1355	57	49.5%	42%
Dichlorocyclopentane	20	50	100	20	20	20	-55°	-30°	400	1.0 (175)	1:475	22%	1355	94	50%	-
Dichlorocyclopentane	20	20	-	80	80	80	-40°	-30°	1000	1.0 (175)	1:146	4%	1355	55	38%	38%
Neopentyl Bromide	5	5	-	20	20	10	-60°	-30°	400	2.0 (120)	1:19	2.6%	1355	139	-	-
Pivaloyl Chloride	10	20	-	30	30	-	-50°	-30°	400	2.0 (60)	1:37	5.5%	1355	148	41%	19.7%
3-pentanone	20	20	-	20	20	-	-20°	-10°	600	2.0 (70)	1:49	5.3%	1355	108	60%	13%
4-Heptanone	20	30	-	20	20	-	-30°	-20°	750	2.0 (165)	1:61	5.0%	1355	81	92%	23%
Cyclopentanone	10	15	20	-	30	30	-40°	-30°	750	2.1 (112)	1:55	4.5%	1355	82	61%	24%

^a 1 ml./min F₂ delivers 2.44 millimoles/hr. F₂^b F₂-pentanoyl Fluoride

TABLE 10

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) $\text{C}_5\text{F}_{10}^{37}\text{Cl}$; 285 (44) $\text{C}_5\text{F}_{10}^{35}\text{Cl}$; 269 (39.7) C_5F_{11} ; 247 (95.5) $\text{C}_5\text{F}_9\text{O}$ or $\text{C}_5\text{F}_8^{35}\text{Cl}$ ($?^{37}\text{Cl}$); 181 (100) C_4F_7 ; 87 (21) $\text{CF}_2^{37}\text{Cl}$; 85 (70) $\text{CF}_2^{35}\text{Cl}$; 69 (38) CF_3 .

EI (70eV): 285 (.3) $\text{C}_5\text{F}_{10}^{35}\text{Cl}$; 269 (20) C_5F_{11} ; 181 (31) C_4F_7 ; 87 (19) $\text{CF}_2^{37}\text{Cl}$; 85 (60) $\text{CF}_2^{35}\text{Cl}$; 69 (100) CF_3 .

^{19}F NMR ($\phi_{\text{CFCl}_3} \equiv 0$ ppm):

$\delta_{\text{CF}_3} = -64.18$ ppm (t)

$J = 10.7$ Hz.

$\phi_{\text{CF}_2\text{Cl}} = -52.29$ ppm (dectet)

F-n-Butyl Chloride:

Infrared (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).

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

CI (CH_4): 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 (50.3) C_4F_9 ; 197 (11.0) $\text{C}_4\text{F}_6^{35}\text{Cl}$; 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 ; 117 (12.0) C_5F_3 ; 105 (10.4) $\text{C}_4\text{F}^{37}\text{Cl}_2$; 103 (67) $\text{CF}^{37}\text{Cl}^{35}\text{Cl}$; 101 (100) $\text{CF}^{35}\text{Cl}_2$; 87 (4.4) $\text{CF}_2^{37}\text{Cl}$; 85 (15.2) $\text{CF}_2^{35}\text{Cl}$; 69 (2.7) CF_3 .

EI (70eV): 219 (11.3) C_4F_9 ; 149 (1.9) $\text{C}_3\text{F}_4^{37}\text{Cl}$; 147 (6.8) $\text{C}_3\text{F}_4^{35}\text{Cl}$; 137 (1.3) $\text{C}_2\text{F}_4^{37}\text{Cl}$; 135 (4.7) $\text{C}_2\text{F}_4^{35}\text{Cl}$; 131 (9.9) C_3F_5 ; 119 (15.0) C_2F_5 ; 100 (11.7) C_2F_4 ; 87 (18.7) $\text{CF}_2^{37}\text{Cl}$; 85 (58.2) $\text{CF}_2^{35}\text{Cl}$; 69 (100) CF_3 .

TABLE 10 (CONTINUED)

^{19}F NMR: ($\phi_{\text{CFCl}_3} \equiv 0$ ppm)	$\text{CF}_3\text{CF}_2-\text{CF}_2-\text{CF}_2\text{Cl}$ a b c d
$\phi_a = -81.7$ ppm (t.t)	$J_{ac} = 9.89$ hz
	$J_{ab} \approx J_{ad} \approx 1.1$ hz
$\phi_b = -126.1$ ppm (t.m)	
$\phi_c = -121.6$ ppm (q.m)	$J_{cd} \approx 1.46$ hz
$\phi_d = -68.9$ ppm (t.q)	$J_{bd} = 12.64$ hz

F-t-Butyl Chloride:

Infrared (cm^{-1}): 1300(sh), 1280(vs), 1195(s), 1162(s), 1070(w), 1042(m), 988(s), 916(m), 863(s), 751(m), 722(ms).

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

CI (CH_4): 237 (24.2) $\text{C}_4\text{F}_8^{37}\text{Cl}$; 235 (77.1) $\text{C}_4\text{F}_8^{35}\text{Cl}$; 220 (4.3) $^{13}\text{C}^{12}\text{C}_3\text{F}_9$; 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) $\text{CF}_2^{37}\text{Cl}$; 85 (11.8) $\text{CF}_2^{35}\text{Cl}$.

EI (70eV): 235 (1.3) $\text{C}_4\text{F}_8^{35}\text{Cl}$; 219 (37.0) C_4F_9 ; 151 (3.8) C_3F_6 ; 149 (1.3) $\text{C}_3\text{F}_4^{37}\text{Cl}$; 147 (4.6) $\text{C}_3\text{F}_4^{35}\text{Cl}$; 131 (15.9) C_3F_5 ; 100 (11.6) C_2F_4 ; 87 (21.6) $\text{CF}_2^{37}\text{Cl}$; 85 (68.0) $\text{CF}_2^{35}\text{Cl}$; 69 (100) CF_5 .

^{19}F NMR: ($\phi_{\text{CFCl}_3} \equiv 0$ ppm)
 $\phi_{\text{CF}_3} = -73.0$ ppm (singlet).

Perfluorocyclopentane:

Infrared: Identical with Literature*

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

CI (CH_4): 131 (100) C_3F_5 ; 121 (16) $\text{C}_2\text{H}_2\text{F}_5$; 103 (14) $\text{C}_2\text{H}_3\text{F}_4$; 100 (21) C_2F_4 ; 81 (69) C_2F_3 ; 69 (29) CF_3 .

*D. G. Weiblen in "FLUORINE CHEMISTRY," Vol II, Ch. 7, p 471, Fig 3, J. H. Simons, Ed., Academic Press, Inc., New York, N.Y., 1954

TABLE 10 (CONTINUED)

EI (70eV): 250 (0.2) C_5F_{10} , M; 181 (24) C_4F_7 ; 131 (100) C_3F_5 , 100 (15) C_2F_4 .

^{19}F NMR ($\phi_{CFC1_3} \equiv 0$ ppm)

$\phi = -132.9$ ppm (singlet)

Chloro-F-cyclopentane:

Infrared (cm^{-1}): 1310(s), 1275(m), 1240(s), 1220(vs), 1120(m), 1065(vw), 1020(m), 970(s), 920(w), 870(s), 740(w).

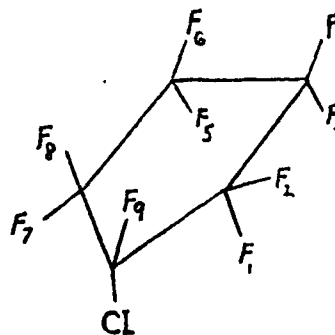
Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 199 (31) $C_4F_6^{37}Cl$; 197 (100) $C_4F_6^{35}Cl$; 159 (12) $C_5H_4F_5$, 149 (29) $C_3F_4^{37}Cl$; 147 (95) $C_3F_4^{35}Cl$; 145 (7.7) $C_4H_2F_5$; 131 (56) C_3F_5 , 123 (21) $C_5H_6F_3$, 103 (27) $C_4H_3F_4$; 100 (11) C_2F_4 ; 83 (14) $C_2H_2F_3$.

EI (70eV): 199(1) $C_4F_6^{37}Cl$; 197 (6.6) $C_4F_6^{35}Cl$; 181 (1.2) C_4F_6 ; 149 (22) $C_3F_4^{37}Cl$; 147 (74) $C_3F_4^{35}Cl$; 131 (100) C_3F_5 ; 118 (3) $C_2F_3^{37}Cl$; 116 (12) $C_2F_3^{35}Cl$; 100 (22) C_2F_4 ; 93 (10) C_3F_3 ; 69 (13) CF_3 , 44 (52) C_2HF , CO_2 .

^{19}F NMR: ($\phi_{CFC1_3} \equiv 0$ ppm)

Two AB Systems and a Singlet.



One AB system belongs to F_1, F_2, F_7, F_8

$\phi = -118.0$ ppm

$J = 262.5$ Hz*

$\phi = -136.53$ ppm

Second AB System belongs to F_3, F_4, F_5, F_6

$\phi = -126.53$ ppm

$J = 253.3$ Hz*

$\phi = -129.0$ ppm

Singlet of multiplets $\phi = -139.8$ ppm.

*A typical geminal coupling constant in a five membered ring system.

TABLE 10 (CONTINUED)

trans-1,2-Dichloro-F-cyclopentane:

Infrared (cm^{-1}): 1340(m), 1300(s), 1250(vs), 1230(vs), 1200(sh,m), 1135(sh,s), 1120(s), 1030(w), 1000(w), 920(s), 870(s), 840(s), 800(s)

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

CI (CH_4): 267 (9.9) *; 265 (63) *; 263 (99) * [typical $^{37}\text{Cl}^{35}\text{Cl}$ pattern, $\text{C}_5\text{F}_7\text{Cl}_2$, M-F]; 249 (4.5) $\text{C}_5\text{F}_8^{37}\text{Cl}$; 247 (15) $\text{C}_5\text{F}_8^{35}\text{Cl}$; 149 (30) $\text{C}_3\text{F}_4^{37}\text{Cl}$; 147 (100) $\text{C}_3\text{F}_4^{35}\text{Cl}$; 131 (23) C_3F_7 ; 119 (12) C_2F_5 ; 117 (13) C_5F_3 ; 118 (6.6) $\text{C}_2\text{F}_3^{37}\text{Cl}$; 116 (21) $\text{C}_2\text{F}_3^{35}\text{Cl}$; 69 (11) CF_3 .

EI (70eV): 149 (31) $\text{C}_3\text{F}_4^{37}\text{Cl}$; 147 (100) $\text{C}_3\text{F}_4^{35}\text{Cl}$; 131 (26) C_3F_5 ; 118 (9.7) $\text{C}_2\text{F}_3^{37}\text{Cl}$; 116 (29) $\text{C}_2\text{F}_3^{35}\text{Cl}$; 93 (10) C_3F_3 ; 69 (15) CF_3

 ^{19}F NMR ($\phi\text{CFCI}_3 \equiv 0$ ppm)

A very complex multiplet of 20+ peaks ranging from -102.92 ppm to -140.09 ppm with apparent couplings of 244, 247 and 256 hz which are typical of geminal couplings in five membered ring systems.

cis-1,2-Dichloro-F-cyclopentane:

Infrared (cm^{-1}): 1330(m), 1300(m), 1240(s), 1210(s), 1100(m), 1040(s), 1000(s), 910(s), 860(s), 820(w).

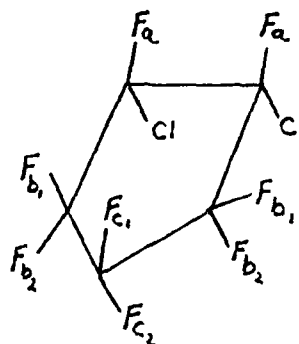
Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 267 (5.4) *; 265 (37) *; 263 (63) * [a typical $^{37}\text{Cl}^{35}\text{Cl}$ pattern for $\text{C}_5\text{F}_7\text{Cl}_2$, M-F]; 249 (4.1) $\text{C}_5\text{F}_8^{37}\text{Cl}$; 247 (14) $\text{C}_5\text{F}_8^{35}\text{Cl}$; 149 (24) $\text{C}_3\text{F}_4^{37}\text{Cl}$; 147 (75) $\text{C}_3\text{F}_4^{35}\text{Cl}$; 97 (35) $\text{C}_3\text{H}_4\text{F}_3$; 93 (11) C_3F_3 ; 81 (26) C_2F_3 ; 77 (66) $\text{C}_2\text{H}_3\text{F}_2$; 69 (55) CF_3 .

EI (70eV): 282 (0.3) $\text{C}_5\text{F}_8^{35}\text{Cl}_2$, M; 149 (32) $\text{C}_3\text{F}_4^{37}\text{Cl}$; 147 (100) $\text{C}_3\text{F}_4^{35}\text{Cl}$; 118 (3.6) $\text{C}_2\text{F}_3^{37}\text{Cl}$; 116 (12) $\text{C}_2\text{F}_3^{35}\text{Cl}$; 69 (14) CF_3 .

TABLE 10 (CONTINUED)

^{19}F NMR ($\phi\text{CFC1}_3 \equiv 0$ ppm)



The ^{19}F NMR pattern consists of two AB type systems F_b and F_c and a singlet of F_a of integrated ratio 2:1:1 respectively.

$$\phi_{F_a} = -137.8 \text{ ppm (s)}$$

$$\phi_{F_b} = -114.8 \text{ ppm and } -126.3 \text{ ppm,}$$

$$J_{AB} = 242.62 \text{ hz}$$

$$\phi_{F_c} = -121.7 \text{ ppm and } -125.1 \text{ ppm,}$$

$$J_{AB} = 250.4 \text{ hz}$$

The reaction product was vacuum line fractionated through -63° , -131°C and -196°C traps. The -196°C trap containing relatively small amounts of CF_4 and other volatiles was discarded. The -131°C trap containing 0.48g of material was glc separated on the phenylmethyl silicone rubber SE-52 column isothermally at 40°C producing 0.43g (29%) F-cyclopentane, (Table 10) 0.025g F-n-butane and 0.02g F-n-pentane. The -63°C trap containing 0.28g of material was glc separated on the Fluorosilicone QF-1 column at 120°C producing two groups of products (B+C). Group B having a retention time of 8-13 minutes and weighing 0.11g was further separated into six components on the QF-1 and SE-52 columns. These compounds have one to four residual hydrogens and were tentatively identified as primarily fluorocyclopentanes. Group C of longer retention times exhibited even less fluorination and were not separated. Aerosol fluorination conditions in this reaction are not optimal and a main carrier flow increase to ~ 1 l/min would raise yields significantly.

Aerosol Fluorination of Chlorocyclopentane: Chlorocyclopentane (Aldrich) was used as received. Its vapor pressure at -10°C (aniline slush) is such that a flow of 135 cc/min of helium through ~ 50 mL of the material contained in a sparge tube evaporator produces a throughput of 2.0 millimole/hr. Details of the aerosol fluorination parameters are given in Table 9. The crude photochemically finished product was vacuum line fractionated (-131°C , 1.30g; -196°C discarded) and the contents of the -131°C trap were separated by gas chromatography on the Fluorosilicone QF-1 column ($10^{\circ}\text{C}/13$ min; $10^{\circ}/\text{min}$ to $60^{\circ}/5$ min; $50^{\circ}/\text{m}$ to $160^{\circ}/5$ min). The major product comprising 49.5% of the -131°C trap contents, 4.3 % yield based on throughput, was F-cyclopentane (12.5%). Two other perfluorinated chloropentanes making up 12.5% and 15.5% of the product collected have not yet been identified.

Aerosol Fluorination of trans-1,2-Dichlorocyclopentane: Trans-1,2-Dichlorocyclopentane was prepared by the method of Gousseron, *et. al.* from cyclopenten.¹⁵ The vapor pressure at 22°C of trans-1,2-dichlorocyclopentane was sufficiently low that a flow of 175 cc/min of helium through ~50 mL of the material contained in the sparge tube evaporator was necessary to obtain a one millimole per hour throughput. The aerosol generator had to be warmed to 40°C to prevent condensation of the product in the aerosol generator and zero yield. Details of the aerosol fluorination parameters are given in Table 9. The photochemically finished product was vacuum line fractionated (-131°C (0.843g), -196°C (0.095g) discarded]. The contents of the -131°C trap were separated gas chromatographically on the Fluorosilicone QF-1 column (10°C/13 min; 10°/min to 60°C; 60°C/7 min then 5°/m to 170°C). The following product distribution [yield] was obtained: 38% [38%] cis/trans-1,2-dichloro-F-cyclopentane, (29% trans/9% cis): 24% [24%] F-chlorocyclopentane; 4% Dichloro-F-pentane; 1.3% chloro-F-pentane; 6% F-cyclopentane, see Table 10 for characterization.

Aerosol Fluorination of Neopentyl Bromide: 1-Bromo-2,2-dimethylpropane was prepared by the method of Wiley, *et. al.* from neopentyl alcohol.¹³ Its vapor pressure at -10°C is such that a flow of 120 cc/min helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 2 millimole/hr. Details of the aerosol fluorination parameters are given in Table 9. Two identical 3.75 hr fluorination runs were carried out differing only in the photochemical finishing (i.e. run #2 uv lamp off). Both sets of 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 min; 2°/m up to 55°C/1 min; 50°/m to 125°/10 min).

The photochemically finished run produced 0.95g of crude product containing elemental bromine with the following product distribution: 40% F-isopentane, 15% 2-methyl-3,3-difluorobutane, 8% 2-fluoro-2-methyl-3,3-difluorobutane, 15% F-isobutane and other unidentified products. See Table II for characterization.

The run without the ultraviolet lamp produced similar quantities of crude product containing elemental bromine with the following product distribution: 10% 2-fluoro-2-methyl-3,3-difluorobutane 20% 2-methyl-3,3-difluorobutane, 20% 1-fluoro-2-methyl-3,3,-difluorobutane and other unidentified products; see Table II for characterization.

Aerosol Fluorination of Pivaloyl Chloride: 2,2-dimethylpropanoyl chloride (Aldrich) was used as received. Its vapor pressure at 0°C is such that a flow of 60 cc/min. helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 0.24g/hr (2 millimoles/hr). Details of the aerosol fluorination parameters are given in Table 9. For a 3 hour, photochemically finished run 0.79g of crude product was collected which when separated on the SE-52 column (0°/5 min; 25°m to 100°/5 min; 25°/min to 200°/15 m) produced 0.32g of F-pivaloyl fluoride in 19.7% yield based on theoretical throughput for a 3 hour run. The product was identical to that produced by LTG fluorination of pivaloyl fluoride.¹⁶

Aerosol Fluorination of 3-Pentanone - Diethyl ketone (Chemical Samples Co.) 99% was used as received. Its vapor pressure at 0°C is such that a flow of 70 cc/min helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 2 millimoles/hr. Details of the aerosol fluorination parameters are given in Table 9. For a four hour, photochemically finished run 0.38g of crude product was separated gas chromatographically on the fluorosilicone QF-1 column (-5°C/2 m; 1°/m to 10°/1 m; 30°/m to

180°/5 m) produced 0.27g of F-3-pentanone (Tables 4 and 5). A 13% yield based on theoretical throughput. It should be noted that significant quantities of unfluorinated 3-pentanone were found inside the reactor upon warming.

Aerosol Fluorination of 4-Heptanone - Di-n-propyl ketone (Aldrich) was used as received. The vapor pressure at 23°C of 4-heptanone was such that a flow of 165 cc/m of helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 2 millimoles/hr. Details of the aerosol fluorination parameters are given in Table 9. For a four hour, photochemically finished run 0.734g of crude product was separated on the Fluorosilicone QF-1 column (30°/1 m; 2°/m to 60°/1 m; 50°/m to 180°/5 m) producing 0.675g F-4-heptanone (92%) with a yield based on theoretical throughput of 23%. Again unfluorinated 4-heptanone was found in the reactor on warming.

Aerosol Fluorination of Cyclopentanone - Cyclopentanone (Aldrich) was used as received. The vapor pressure of cyclopentanone at 23°C is such that a flow of 112 cc/m helium through 50 mL of the material contained in a sparge tube evaporator produces a throughput of 2.1 millimoles per hour. Details of the aerosol fluorination parameters are given in Table 9. For a 3 hour, photochemically finished reaction, 0.62g of crude product was separated on the Fluorosilicone QF-1 column (10°/1 m; 1°/m to 30°/1 m; 20°/m to 100°/10 m) producing 0.378g of F-pentanoyl fluoride (61%) with a yield based on theoretical throughput of 24%. Cyclopentanone was again found in the reactor on warming.

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APPENDIX I

Low-Temperature Fluorination of Aerosol Suspensions of Hydrocarbons Utilizing Elemental Fluorine

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Abstract: This work describes a new concept in direct fluorination methodology and an apparatus designed to achieve conditions necessary for the rapid, continuous partial or complete fluorination of hydrocarbon molecules under controlled conditions of temperature and concentration. Results from the fluorination of neopentane are presented which indicate that although the degree of fluorination for a given set of conditions indicates a Gaussian distribution, investigation of specific isomers indicates significant deviations from statistical isomer distributions in fluorinated neopentanes. Photochemical assisted fluorinations of neopentane, 1,4-dioxane, cyclohexane, and 2,2-dimethyl-1,3-dioxolane are described which produce the perfluorinated analogues directly in good purity and in high yields.

The fluorination of hydrocarbon molecules by present technology is limited to a few distinct methodologies. In most cases the most appealing methods from the standpoint of reaction rate and scale-up operate in anhydrous hydrogen fluoride which reacts with many organic moieties (Swart's halogen-exchange reaction and Simon's electrochemical process),¹⁻³ utilize metal fluoride

reagents which are expensive (AgF_2 , HgF_2), give incomplete fluorination with increasing complexity of the structure of the molecule to be fluorinated (CoF_3 , KCoF_4)^{4,7} or operate at elevated temperatures, and produce generally lower yields of more complex molecules (Bigelow's "jet fluorination").⁸⁻¹⁰ The "LaMar"

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method developed by Lagow and Margrave¹¹⁻¹³ utilizes "long" reaction times and the high dilution of fluorine with helium which also acts as a heat sink. A later development in this process by Lagow, Maraschin, and Adcock¹⁴⁻¹⁸ couples the high dilution and "long" reaction time with a low-temperature-gradient (LTG) reactor densely packed with "light" copper turnings. The "LTG" method produces good yields of highly branched fluorocarbons^{14,15} and is generally useful for the fluorination of hydrocarbon ethers,¹⁶ esters,¹⁷ acid fluorides,^{17,18} acid anhydrides,¹⁹ and cyclic amines.²⁰ It, however, works well only for molecules with appreciable solid-state volatility and crystallinity. Materials that form oils and glasses or have low solid-state volatility give considerably lower yields than the 30-80% yields obtained when more nearly ideal molecules are fluorinated. It is also a batch process which is generally suitable only for small scale syntheses.

All of the previously mentioned methodologies have serious limitations, and although some have been adopted for industrial scale production, clearly a simple, more nearly general fluorination method would be desirable. We would like to present what we believe is such a method.

Description of the Process

The significant successes of the LTG direct fluorination technique and the intrinsic simplicity of direct fluorination have led to a firm belief that a successful, general fluorination technique could be developed employing elemental fluorine. A critical analysis of the LTG reaction system produced a set of five conditions which we believe contribute to a high yield reaction. The conditions which we considered important are (a) fluorination of molecules in the crystalline state, (b) a very high reactant surface area exposed to gaseous fluorine, (c) low initial temperatures, (d) high initial dilution of fluorine gas, and (e) a highly efficient mechanism of heat dissipation.

The crystalline matrix reduces hydrocarbon radical recombinations when radicals are formed under "dilute" conditions. The crystalline matrix acts as an energy sink to dissipate reaction energies. A high reactant surface area promotes uniform attack by fluorine on all reactant molecules. Low temperatures reduce the vigor of reaction by an overall reduction in kinetic energy and by limiting the number of radical chain initiations. High initial dilution of fluorine reduces the overall reaction rate and reduces the likelihood of simultaneous attack by two fluorine molecules or radicals on adjacent sites on a molecule which would increase the degree of fragmentation. Effective heat dissipation would prevent the formation of "hot spots" and prevent combustion from occurring.²¹

These conditions, however, must be modified if one is to achieve high degrees of fluorination over a reasonable time span. The concentration of fluorine must be increased to maintain a good reaction rate as the reactant molecules become more highly fluorinated and a greater percentage of collisions are ineffective. It is also beneficial in this regard to increase the temperature. Since these conditions directly conflict with the desired initial conditions, their imposition must be separated in time or in space. The LTG system simply changes the applied temperature gradient and increases the fluorine concentration over time.

Separation of the perfluorination enhancing conditions from the initial conditions in space requires that the reactant be mobile. This mobile species may then be induced to pass through progressively warmer regions which have higher degrees of fluorine concentration. A gaseous reactant would be mobile, of course, but the desirability of limiting collisions between hydrocarbon radicals and thus limiting coupling reactions giving tars and oils dictates a condensed, preferably crystalline, phase. A liquid reagent stream does not allow for the uniform, rapid mixing of the very reactive gaseous elemental fluorine, thus preventing uniform, controlled attack and substitution of fluorine at every C-H bond.

In order to achieve gaslike mobility and retain crystallinity, it is necessary to produce extremely small solid particulates. These particulates may then be suspended and transported by using a carrier gas. These particulates possess extremely high surface area which permits uniform attack by gaseous elemental fluorine on the suspended reactant. Extremely effective heat dissipation may be achieved by using helium as the carrier. Multiple collisions of the reactant particulates with the helium carrier gas molecules dissipate heat rapidly. Excess energy is continuously carried by the helium atoms to the walls of the reactor.

Principles of aerosol production are well developed. Our initial design ideas were developed from study of existing technology for producing aerosols which were developed primarily as an adjunct of atmospheric and industrial hygiene studies. Descriptive passages by N. A. Fuchs and A. G. Sutugin,²² R. D. Cadle,²³ and F. C. Goodrich²⁴ describe the requirements of generators capable of producing aerosols. A more recent paper by A. G. Sutugin describes a mixer-type generator which is generally applicable to the problem of steady-state aerosol production in a flow reactor.²⁵ The major difference between our own independently developed design and that described by Sutugin is the subambient temperature capability of our design and its incorporation into a flow-type reactor system.

The aerosol fluorination system designed to produce a controlled continuous stream of aerosol particulates includes the following components (Figure 1). A bed of sodium fluoride heated to 850 °C (A) sublimates highly dispersed NaF particles (average radius 17.5 Å²⁶) into the helium carrier gas. These particles serve as condensation nuclei for the hydrocarbon condensation. The carrier gas is chilled to near -196 °C by passing through a liquid-nitrogen-cooled heat exchanger (B). The chilled carrier gas, helium in this embodiment, is mixed with a second gas stream containing the hydrocarbon vapor in a precise arrangement within the body of the generator (C). The hydrocarbon vapor in the stream produced by an evaporator device (D) will condense into aggregates around the sodium fluoride particles within the chilled carrier. The chilled aerosol is directly channeled into the reactor (E) where it is mixed with elemental fluorine in such a way as to produce uniform contact between the aerosol particles and elemental fluorine. The temperature of the reactor (E) is controlled by means of an integral heat exchanger which can provide variable temperatures from the cryogenic to the ambient range.

The aerosol generator system is of the evaporation-condensation type. It, however, seems likely that aerosol particulates generated by any mechanism, physical, chemical, or mechanical, would work equally well. It is the high surface area created by extensive subdivision of aggregates that is essential to the process.

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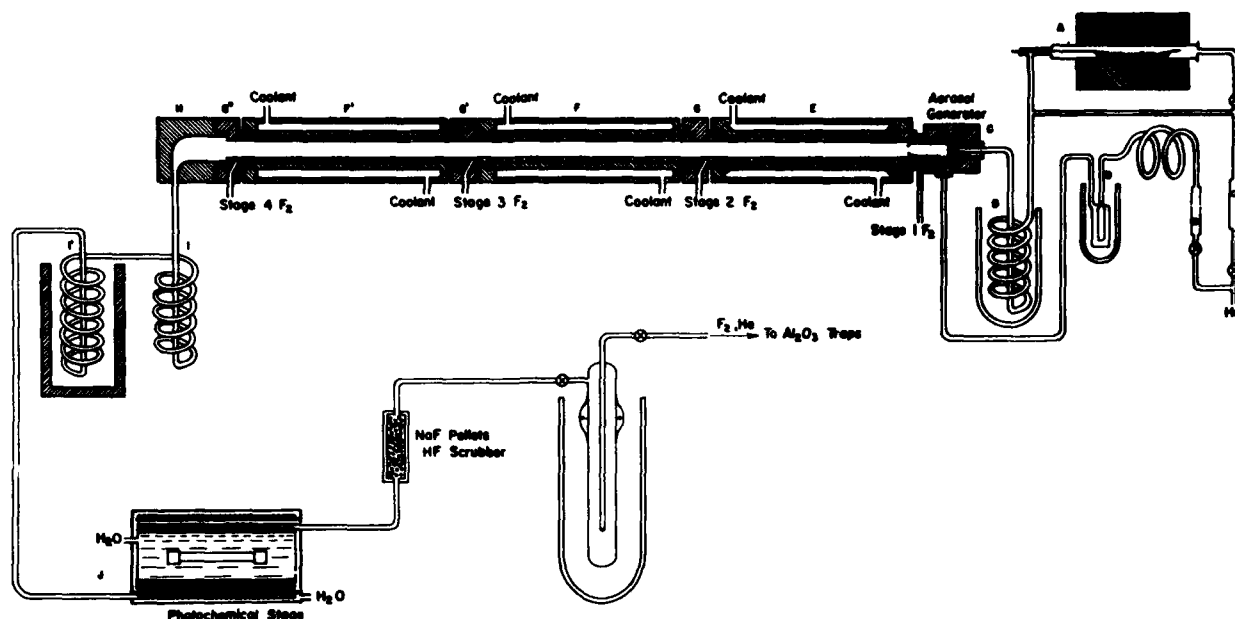


Figure 1. Aerosol fluorinator.

Having created a mobile reactant, it is possible to separate in space the conditions giving low fragmentation, i.e., high initial dilution of fluorine and low temperature, from those conditions leading to high degrees of fluorination, i.e., increased fluorine concentration and temperature.

Modular design of the system has allowed for the addition of staging components following the reactor (E). Each staging component consists of a module (F) and a "staging insert" (G). A series of modules (F') connected to the reactor thus provide for independently controlled-temperature zones, and the addition of "staging inserts" (G') allows the independently controlled injection of additional elemental fluorine. With use of these devices, hydrocarbon or other molecules may be controllably fluorinated to any degree including perfluorination. It is also conceivable that other reagents besides elemental fluorine can be introduced in the later stages to achieve functionalization etc.²⁷⁻²⁹

The addition of modules and staging inserts may be continued indefinitely by insertion ahead of the end cap (H). Each stage may be modified to provide for recycling of any or all of the various reacting species although this is not practical at the lab scale. In the system shown (Figure 1), a total of three staging inserts have been assembled, giving in effect a four-stage aerosol fluorination reactor in which fluorine can be added in four independently controlled zones at three independently controlled temperatures.³⁰

In molecules which are exceptionally difficult to perfluorinate, a heated coil (I') and/or a water-cooled flow-type photochemical reaction stage (J) following stage 4 (Figure 1) has been utilized to significantly activate the elemental fluorine and increase the reactant contact time before quenching. The photochemical stage allows exceptionally high yields of perfluorinated products as well as much more efficient utilization of elemental fluorine. Recent results exhibit perfluorination of neopentane using a 20% excess of fluorine.

The multistaged aerosol fluorination reactor achieves near optimum control over the potentially violent direct fluorination

reaction. It is possible to expose the unfluorinated reactant to a very dilute, even distribution of elemental fluorine at low temperatures. Furthermore the condensed phase of the aerosol particle distributes reaction heat evenly over a large number of molecules held in an ideally crystalline aggregate which may readily dissipate energy by multiple rapid collisions with helium gas. All of these effects serve to reduce the violence and heat accumulation which are primary concerns in direct fluorination. As the reactant molecule becomes more highly fluorinated and hence less vulnerable, the aerosol aggregate is carried into regions of higher fluorine concentration, higher temperature, and generally more rigorous conditions which tend to bring about higher degrees of fluorination. Finally the highly fluorinated product mixture may be introduced into the photochemical stage to achieve maximum fluorination.

This combination of conditions, which allows independent control of reactant concentration, stoichiometry, temperature, and reaction time, is unique to the aerosol fluorination reactor. It is in effect a dynamic, variable-fluorine-concentration-gradient, variable-temperature-gradient reactor.

Description of the Experiments

Neopentane was purchased from K and K Laboratories, Inc., and was used as received. 1,4-Dioxane and cyclohexane (Fisher) were dried over Linde 4-A molecular sieve before use. 2,2-Dimethyl-1,3-dioxolane was prepared by allowing a 1:2 molar mixture of acetone-ethylene glycol to reflux over L-4A molecular sieve in the presence of paratoluene sulfonic acid for several days. The filtered liquid was run slowly into saturated aqueous potassium carbonate. The separated organic (top) layer was dried over L-4A sieves and fractionally distilled by using a spinning band distillation apparatus. The pure product (bp 89.0–90.0 °C, lit.³¹ 90.0 °C) was collected in 11% yield although much more was collected as an apparent acetone azeotrope.

Elemental fluorine was purchased from Air Products Co. (97% technical grade, low oxygen content) in a cylinder containing 4.9 lb of F₂ at 400 psig. IR spectra were run on a Perkin-Elmer 257 grating spectrophotometer; mass spectra (electron-impact and chemical ionization) were obtained on a Hewlett-Packard 5980A mass spectrometer. ¹H and ¹⁹F NMR were obtained from the South Carolina Magnetic Resonance Facility, Columbia, SC, operating under Grant NSF-CHE78-18723. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Mass throughput values for neopentane, 1,4-dioxane, 2,2-dimethyl-1,3-dioxolane, and cyclohexane were calculated from empirical data.³⁰ Gas chromatographic separations were made on a Bendix Model 2300 gas chromatograph with multilinear programming

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Table I. ¹⁹F NMR Data of Fluorinated Neopentanes

formula	ref no.	structure	CF ₃	CF ₂ H		CFH ₂		integratn ratios
			φ,° ppm	φ,° ppm	J, Hz	φ,° ppm	J, Hz	
C ₅ H ₁₂	*	C(CH ₃) ₄						
C ₅ H ₁₁ F	ND	(CH ₃) ₃ C-CFH ₂				222.7 (t)	46	
C ₅ H ₁₀ F ₂	NL	(CH ₃) ₃ C(CFH ₂) ₂				227.8 (t)	50.9	
C ₅ H ₉ F ₃	NF'	(CH ₃) ₃ C-CF ₂ H		~128 ^b (d)	57.1			
C ₅ H ₈ F ₄	NQ	(CFH ₂) ₃ C-CH ₃				234.6 (t)	49.6	
C ₅ H ₇ F ₅	NK'	(CH ₃) ₂ C(CFH ₂) ₂ (CF ₂ H)		~131 ^b (d)	53.4	~228 ^b (t)	45.8	d:t ≈ 2:1
C ₅ H ₆ F ₆	NS	C(CFH ₂) ₄				240.1 (t)	45.8	
C ₅ H ₅ F ₇	NN	(CH ₃) ₂ C(CF ₂ H) ₂		129.2 (d)	53.4			
C ₅ H ₄ F ₈	NO	(CFH ₂) ₃ C(CF ₂ H)(CH ₃)		132.7 (d)	53.4	236.3 (t)	45.8	d:t ≈ 1:1
C ₅ H ₃ F ₉	NT	(CFH ₂) ₃ C-CF ₂ H		131.1 (d)	53.4	241.1 (t)	45.8	d:t ≈ 2:3
C ₅ H ₂ F ₁₀	NR	(CFH ₂) ₂ C(CF ₂ H) ₂		130.1 (d)	48.8	242.4 (t)	48.8	d:t ≈ 2:1
C ₅ H ₁ F ₁₁	NP	(CF ₂ H) ₂ C-CFH ₂		129.1 (d)	53.4	243.8 (t)	45.8	d:t = 6.8:1
C ₅ H ₀ F ₁₂	NK	C(CF ₂ H) ₄		128.4 (d)	53.4			
C ₄ H ₉ F ₃	NI	(CF ₂ H) ₂ C(CF ₃) ₂ (CFH ₂)	66.8 (s)	129.3 (d)	51	244.4 (t)	41	s:d:t = 3:4:1
C ₄ H ₈ F ₄	NH	(CF ₂ H) ₂ C-CF ₃	64.5 (s)	127.8 (d)	51			s:d = 1:2
C ₄ H ₇ F ₅	NG	(CF ₃) ₂ C(CFH ₂) ₂ (CF ₂ H)	66.57 ^c (q)	130.1 ^c (d)	52.2	240.4 ^c (t)	45.6	
C ₄ H ₆ F ₆	NE	(CF ₂ H) ₂ C(CF ₃) ₂	64.6 ^c (p)	127.29 (d)	54.5			
C ₄ H ₅ F ₇	NC	(CF ₃) ₂ C-CF ₂ H	65.4 ^c (t)	125.7	53			
C ₄ H ₄ F ₈	NB	C(CF ₃) ₄	65.42 ^c (s)					

^a Chemical shifts φ (ppm) are relative to internal CFCl₃; since resolution of the spectra was not very high, only the large geminal F-H couplings were observed. ^b Chemical shift values measured from spectra. ^c Data from LTG products; chemical shifts are measured from spectra. See ref 14 and 37.

and TC detection. The photochemical reaction stage consisted of 10 m of 0.015-in. wall, 3/8-in. ID FEP Teflon tubing, one layer wrapped around a 50 mm × 390 mm quartz immersion well containing a 550-W (Hanovia) medium-pressure mercury arc lamp and a second layer wrapped concentrically about an overlying 75-mm Pyrex tube. All FEP Teflon tubing is maintained at approximately 20–25 °C by positive water circulation over all surfaces.

Neopentane Reactions. Reactions F/N-1 through F/N-7 were run on a two-stage modification of the aerosol reactor. This reactor consisted of the reactor with stage-two insert, one staging module without insert followed by the end piece, H, and connecting tubing (3/8-in. copper tubing). The active volume of this reactor was 321 cm³ with average diameter of less than 0.5 in. Reaction times were approximated by dividing the active volume of the reactor by the combined flows of gas, principally helium.

Reactions F/N-8 through F/N-12 were run on a four stage modification of the aerosol reactor. This reactor consisted of the reactor with stage-two insert, two staging modules each fitted with staging inserts followed by the end piece, and connecting tubing. The active volume of this reactor was 268 cm³. The reduced volume is a result of the volume displacement of the second staging insert absent in the first staging module in the previous configuration.

Reactions F/N-13 through F/N-21 were run on the four-stage modification extended by the addition of a 10 m × 3/8 in. copper coil which increased the active volume of this reactor to 771 cm³. A 15-m coil of 3/8-in. copper tubing and (or) the photochemical module pictured in Figure 1 were the final extensions increasing the active volumes to 1524 and 2108 cm³ (or 1355 cm³), respectively. Their effect on reaction times are proportional to the volume changes; however, their effects on product distributions are not nearly so marked as that produced by the first coil. Detailed reaction conditions for each reactor modification are compiled elsewhere.^{30c}

In multistaging experiments a gradient in fluorine concentrations was used. For the reactions illustrated in Figures 2–5 an approximate fluorine concentration profile is given in the diagrams of the product distributions. These concentration profiles were calculated by dividing the fluorine flow by the total flow at the end of each reactor stage. Thus they represent the concentrations one would find at these points if no reaction was to occur. The true steady-state fluorine concentration is certainly lower than this value as a result of reaction; the discrepancy will be larger for reactions with high hydrocarbon/fluorine ratios.

The reaction time indicated in these diagrams (Figures 2–5) is the average time required by a suspended hydrocarbon particle travelling from the aerosol generator to the product collecting trap where the fluorination is quenched at -196 °C. This time was calculated from the volume of the reactor and the sum of flows through it. Of course this is only correct if the hydrocarbon remains suspended while it is inside the reactor.

Product mixtures from all neopentane fluorinations were treated with NaF/molecular sieves to remove residual HF. For a check on the performance of every reaction, an analytical GLC injection of a solution of the product mixture in CCl₄ was separated on a 3/8 in. × 7 m 13%

fluorosilicone QF-1 (Analabs) on 60–80 mesh chromosorb p column. The following temperature program was used: T₁ = 25 °C for 10 min, R₁ = 10°/min; T₂ = 75 °C for 10 min, R₂ = 50°/min; T₃ = 125 °C for 24 min.

For identification of the unknown partially fluorinated neopentanes, identical samples from different reactions (as certified byIR) were combined to obtain sufficient material for NMR measurements (Tables I and II), mass spectra, and elemental analysis (supplementary material, Table A). Compounds are ordered NA, NB, ..., NT on the basis of their fluorosilicone QF-1 column retention times (Table III).

Only one fraction from the fluorosilicone QF-1 GLC-separations was further separated. The peak between 33- and 35-min retention time (NO, NP) was separated on a 3/8 in. × 4 m 10% SE-52 phenyl-methylsilicone rubber (Analabs) on 60–80 mesh chromosorb p column by using the following temperature program: T₁ = 70 °C for 10 min, R₁ = 25°/min; T₂ = T₃ = 120 °C for 7 min. Compounds NS and NT occurred in some reactions as a difficult to separate mixture but could be produced nearly pure by stoichiometric control. All purified products prepared for elemental analysis were assayed on the SE-52 column to establish purity after initial QF-1 column GLC purification.

The product distributions for some typical reactions were estimated by determining the areas of peaks in the GLC traces; these data are compiled in Table IV. Since no decomposition during workup was observed and all materials were volatile and soluble in CCl₄, these normalized values should represent something close to the true relative product distributions for the neopentane fluorinations under different reaction conditions. Combining isomers these distributions displayed graphically (Figure 2) show the effect of reaction parameters on fluorination efficiency.

Photochemical Neopentane Reactions. Procedures for conducting the photochemical neopentane reactions (Figure 3) were very similar to the "dark" reactions. As previously was the case, the particulate furnace, cooling jackets, carrier flows, fluorine flows, and, where used, the photochemical cell were allowed to come to equilibrium readiness before any hydrocarbon was admitted to the system. The details of typical photochemical experimental conditions for neopentane, 1,4-dioxane, 2,2-dimethyl-1,3-dioxolane, and cyclohexane are given in Table V, others are detailed elsewhere.^{30c} A set of control runs (NPF/N-3 through NPF/N-7) were run under identical conditions except that the photochemical lamp was off. The product distributions of two control runs (NPF/N-3 and NPF/N-6) are illustrated in Figure 3 along with the photochemical runs.

The problems of mass balance in the aerosol system are complex. Through-puts are determined empirically by collecting the output of the hydrocarbon evaporator over several half-an-hour periods. A calibration curve is developed as a function of carrier flow vs. mass output for a given reservoir temperature. Except for those reactions giving only a few products, yields are tedious, time consuming, and prone to experimentalist technique losses. Product distributions as given can be deceiving in that they are yields relative to other products. Generally output masses are about two-thirds of those expected even when no fluorine is used. This points out one of the difficulties of aerosol particulates, i.e., their capture.

Table II. ^1H NMR Spectra of Fluorinated Neopentanes^a

formula	ref no.	structure	CH_3		CH_2F		CHF_2		integratn ratios
			δ	$J, ^\circ\text{Hz}$	δ	$J, ^\circ\text{Hz}$	δ	$J, ^\circ\text{Hz}$	
C_5H_{12} ^c	*	$\text{C}(\text{CH}_3)_4$	0.94						
$\text{C}_5\text{H}_{11}\text{F}$	ND	$(\text{CH}_3)_3\text{C}-\text{CFH}_2$	0.96 (d)	1.7	4.0 (d)	48			
$\text{C}_5\text{H}_{10}\text{F}_2$	NL	$(\text{CH}_3)_3\text{C}(\text{CFH}_2)_2$	0.96 (t)	1.8	4.2 (d)	47.6			t:d = 3:2
$\text{C}_5\text{H}_9\text{F}_3$	NF'	$(\text{CH}_3)_3\text{C}-\text{CF}_2\text{H}$	0.99 (d)	1			~7 ^c		
$\text{C}_5\text{H}_8\text{F}_4$	NQ	$(\text{CFH}_2)_3\text{C}-\text{CH}_3$	1.05 (q)	1.7	4.4 (d)	47.1			g:d = 1:2
$\text{C}_5\text{H}_7\text{F}_5$	NK'	$(\text{CH}_3)_2\text{C}(\text{CFH}_2)(\text{CF}_2\text{H})$	1.06 (m)	<1	4.25 (d)	47.1	5.67 (t)	56.6	m:d:t = 7:2:1
$\text{C}_5\text{H}_6\text{F}_6$	NS	$\text{C}(\text{CH}_2\text{F})_4$			4.6 (d)	46.6			
$\text{C}_5\text{H}_5\text{F}_7$	NN	$(\text{CH}_3)_2\text{C}(\text{CF}_2\text{H})_2$	1.3				~6 (t)		s:t = 3:1
$\text{C}_5\text{H}_4\text{F}_8$	NO	$(\text{CFH}_2)_2\text{C}(\text{CF}_2\text{H})(\text{CH}_3)$	1.1		m ^e		5.8 (t)	55.7	s:m:t = 3:4:1
$\text{C}_5\text{H}_3\text{F}_9$	NT	$(\text{CFH}_2)_3\text{C}-\text{CF}_2\text{H}$			4.66 (d)	46.6	6.0 (t)	54.7	d:t = 6:1
$\text{C}_5\text{H}_2\text{F}_{10}$	NR	$(\text{CFH}_2)_2\text{C}(\text{CF}_2\text{H})_2$			4.7 (d)	46.4	6.1 (t)	54.4	d:t = 2:1
$\text{C}_5\text{H}_1\text{F}_{11}$	NP	$(\text{CF}_2\text{H})_3\text{C}-\text{CFH}_2$			4.9 (d)	46.1	6.2 (t)	54.2	
$\text{C}_5\text{H}_0\text{F}_{12}$	NK	$\text{C}(\text{CF}_2\text{H})_4$					6.3 (t)	54	
$\text{C}_5\text{H}_1\text{F}_{11}$	NI	$(\text{CF}_2\text{H})_3\text{C}(\text{CF}_2\text{H})(\text{CFH}_2)$			4.95 (d)	46	6.24 (t)	54	
$\text{C}_5\text{H}_0\text{F}_{12}$	NH	$(\text{CF}_2\text{H})_3\text{C}-\text{CF}_2$					6.3 (t)	53	
$\text{C}_5\text{H}_1\text{F}_{11}$	NG	$(\text{CF}_2)_2\text{C}(\text{CFH}_2)(\text{CF}_2\text{H})$			4.92 (d)	45.6	6.31 (t)	52.2	f
$\text{C}_5\text{H}_0\text{F}_{12}$	NE	$(\text{CF}_2)_3\text{C}(\text{CF}_2\text{H})_2$					6.21 (t)	52.2	f
$\text{C}_5\text{H}_1\text{F}_{11}$	NC	$(\text{CF}_2)_3\text{C}-\text{CF}_2\text{H}$					6.255 (t)	54.5	f
C_5F_{12}	NB	$\text{C}(\text{CF}_3)_4$							

^a Chemical shifts δ are relative to Me_4Si ; they were calculated by assuming that the residual proton on CDCl_3 occurs at 7.26 on δ scale. ^b d = doublet, t = triplet, q = quadruplet, m = multiplet (note only basic splittings are given). ^c This signal is a very weak triplet, which does not appear in the print out. ^d From: F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York and London, 1969. ^e Complex multiplet between 4.3 and 4.6 ppm. ^f Data from LTG products, see ref 14 and 37.

Table III. Identities of Products from Neopentane Fluorinations

ref no.	structure	name
NA	$\text{F}-\text{C}(\text{CF}_3)_3$	perfluoroisobutane
NB	$\text{C}(\text{CF}_3)_4$	perfluoroneopentane ^{14,32}
NC	$\text{CF}_3\text{H}-\text{C}(\text{CF}_3)_3$	undecafluoroneopentane ³²
ND	$\text{CFH}_2-\text{C}(\text{CH}_3)_3$	$\equiv$ 1-hydryl-F-neopentane
NE	$(\text{CF}_2\text{H})_2\text{C}(\text{CF}_3)_2$	1-fluoroneopentane
NF'	$\text{CF}_3\text{H}-\text{C}(\text{CH}_3)_3$	sym decafluoroneopentane ³²
NG	$\text{CFH}_2-\text{C}(\text{CF}_2\text{H})(\text{CF}_3)_2$	$\equiv$ 1,3-dihydryl-F-neopentane
NH	$\text{CF}_3\text{C}(\text{CF}_2\text{H})_3$	1,1-difluoroneopentane
NI	$\text{CF}_3-\text{C}(\text{CFH}_2)(\text{CF}_2\text{H})_2$	sym nonafluoroneopentane
NK	$\text{C}(\text{CF}_2\text{H})_4$	$\equiv$ 1,1,1,3,3-pentafluoro-2,2-bis-(difluoromethyl)propane
NK'	$\text{CF}_3\text{H}-\text{C}(\text{CFH}_2)(\text{CH}_3)_2$	asym octafluoroneopentane
NL	$(\text{CH}_3)_3\text{C}(\text{CFH}_2)_2$	$\equiv$ 1,1,1,3-tetrafluoro-2,2-bis-(difluoromethyl)propane
NN	$(\text{CF}_2\text{H})_2\text{C}(\text{CH}_3)_2$	sym octafluoroneopentane
NO	$\text{CF}_3\text{H}-\text{C}(\text{CH}_3)(\text{CFH}_2)_2$	$\equiv$ 1,1,1,3,3-tetrafluoro-2,2-bis-(difluoromethyl)propane
NP	$(\text{CF}_2\text{H})_3\text{C}-\text{CFH}_2$	asym or 1,1,3-trifluoroneopentane
NQ	$(\text{CFH}_2)_3\text{C}-\text{CH}_3$	sym or 1,3-difluoroneopentane
NR	$(\text{CFH}_2)_2\text{C}(\text{CF}_2\text{H})_2$	$\equiv$ 1-fluoro-2,2-bis(fluoromethyl)-propane
NS	$\text{C}(\text{CFH}_2)_4$	hexafluoroneopentane
NT	$\text{CF}_3\text{H}-\text{C}(\text{CFH}_2)_3$	$\equiv$ 1,1,3,3-tetrafluoro-2,2-bis-(fluoromethyl)propane
*	$\text{C}(\text{CH}_3)_4$	sym tetrafluoroneopentane
		$\equiv$ 1,3-difluoro-2,2-bis(fluoromethyl)-propane
		pentafluoroneopentane
		$\equiv$ 1,1,3-trifluoro-2,2-bis(fluoro-methyl)propane
		unreacted neopentane (2,2-dimethylpropane)

Yields of the photochemical experiments leading to a few products are given. Reaction PF/N-7 yields 0.54 g of F-neopentane for 5 h 1 mmol/h run. Theoretical yield estimate for 5 mmol is 1.44 g, a yield of 38%.

Table IV. Product Distributions from Selected Aerosol Fluorinations of Neopentane (Estimated from Peak Areas of GLC Traces)

	F/N-1	F/N-6	F/N-7	F/N-11	F/N-16	F/N-17	F/N-20	F/N-21
NA	4.0	0.5	0.3					
NB						0.3	4.0	4.0
NC						0.6	9.2	9.0
ND	21.8	7.6	3.2			4.4	24.0	19.4
NE					0.7	11.2	32.6	18.6
NF'	4.3	2.5	1.6					
NG					4.1	5.1	3.3	5.0
NH					3.9	18.9	20.8	14.7
NI					15.7	17.4		10.3
NK'	10.7	10.1	8.7					
NK					12.4	18.7	6.2	10.2
NL	37.9	20.1	10.3					
NM				4.6	9.6	3.5		1.5
NN				1.6	1.5			
NO	6.5	17.4	23.9	14.7	7.4			
NF		2.8	3.8	14.3	6.4			
NP		0.9	1.3	6.1	18.1	15.2		6.5
NR	12.8	16.2	14.0	2.2				
NS	1.8	4.1	7.6	24.7	14.9	3.5		0.7
NT		(3.6)	(5.1)					
		17.8	25.3					
		(14.2)	(20.2)	31.8	5.3	1.3		

^a Unreacted neopentane.

1,4-Dioxane Reactions. Although many reactions involving all levels of fluorination of 1,4-dioxane were performed,³⁰ the instability of the polyfluoro-1,4-dioxanes, especially the trifluoro species, prevented as detailed an examination of product distributions as was detailed for neopentane. Only those reactions (Table V) producing high degrees of fluorine substitution were amenable to even near quantitative workup. In each case the products collected were condensed into a reservoir containing sodium fluoride pellets and L-4A molecular sieves separated by a 1-in. layer of "light" copper turnings and allowed to stand at room temperature overnight. The products remaining were vacuum line fractionated through -78, -131, and -196 °C traps. The -78 and -131 °C traps were combined and subjected to gas chromatographic separation on the fluorosilicone QF-1 column described earlier at a constant temperature of 125 °C. The -196 °C trap, usually containing only a few milligrams of very volatile material, was discarded.

Products from the fluorinations of 1,4-dioxane have been characterized by their ^{19}F and ^1H NMR spectra, CI and EI mass spectra, and IR spectra. As is also the case for partially fluorinated cyclohexanes, ^1H NMR spectra of partially fluorinated 1,4-dioxanes are very complex due

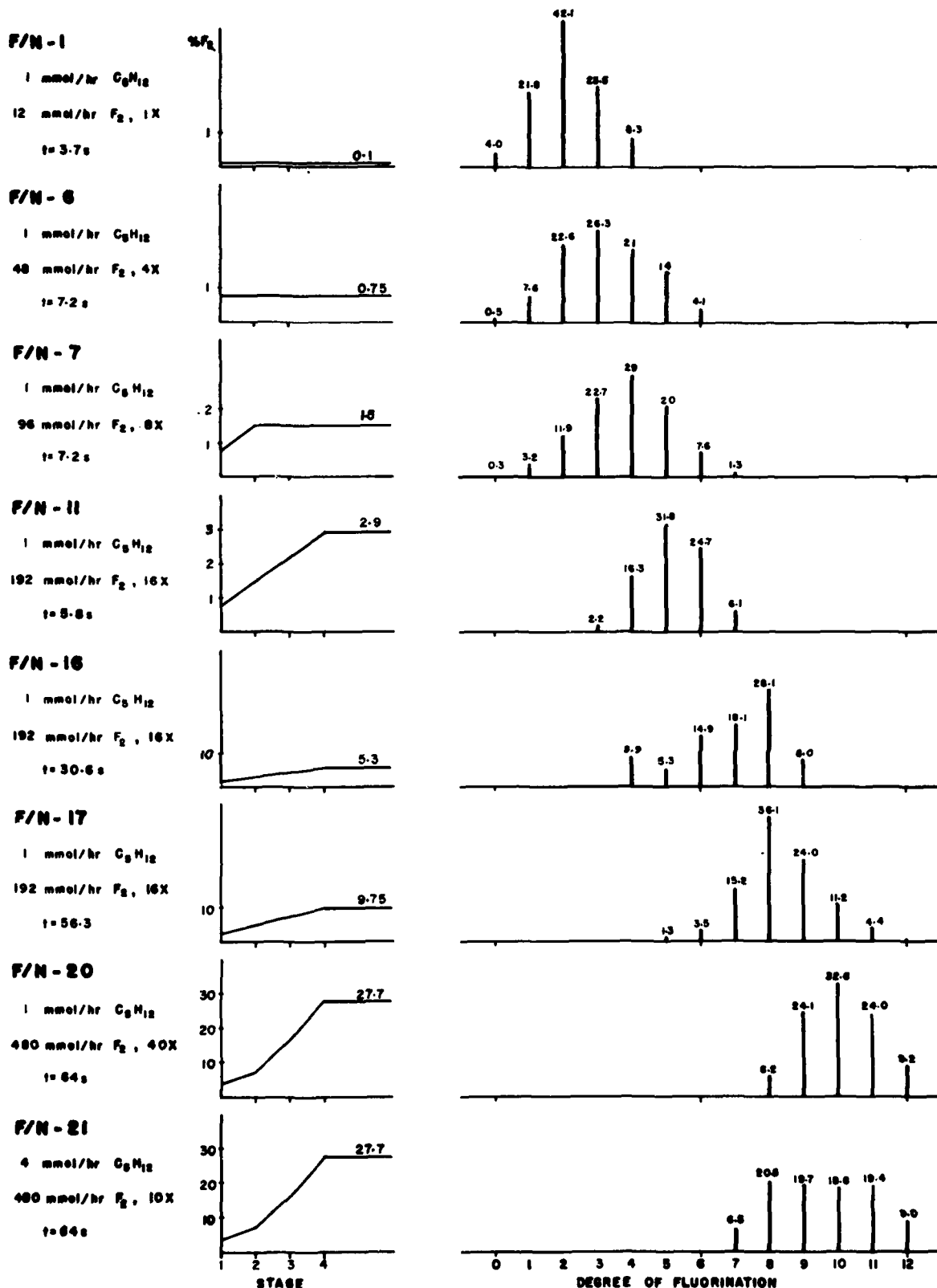


Figure 2. Neopentane product distributions.

to coupling across the ring. But again signals of CH_2 groups and signals of CFH groups can be clearly distinguished, and their relative integrations give information about the extent of fluorination.^{30,31} ^{19}F NMR spectra are somewhat less complex. ^{19}F NMR spectra for both the fully and partially fluorinated 1,4-dioxanes containing four or more fluorine

atoms have been described in detail in the literature simplifying characterization.^{7,32}

(32) J. Burdon and I. W. Parsons, *Tetrahedron*, 27, 4553 (1971).

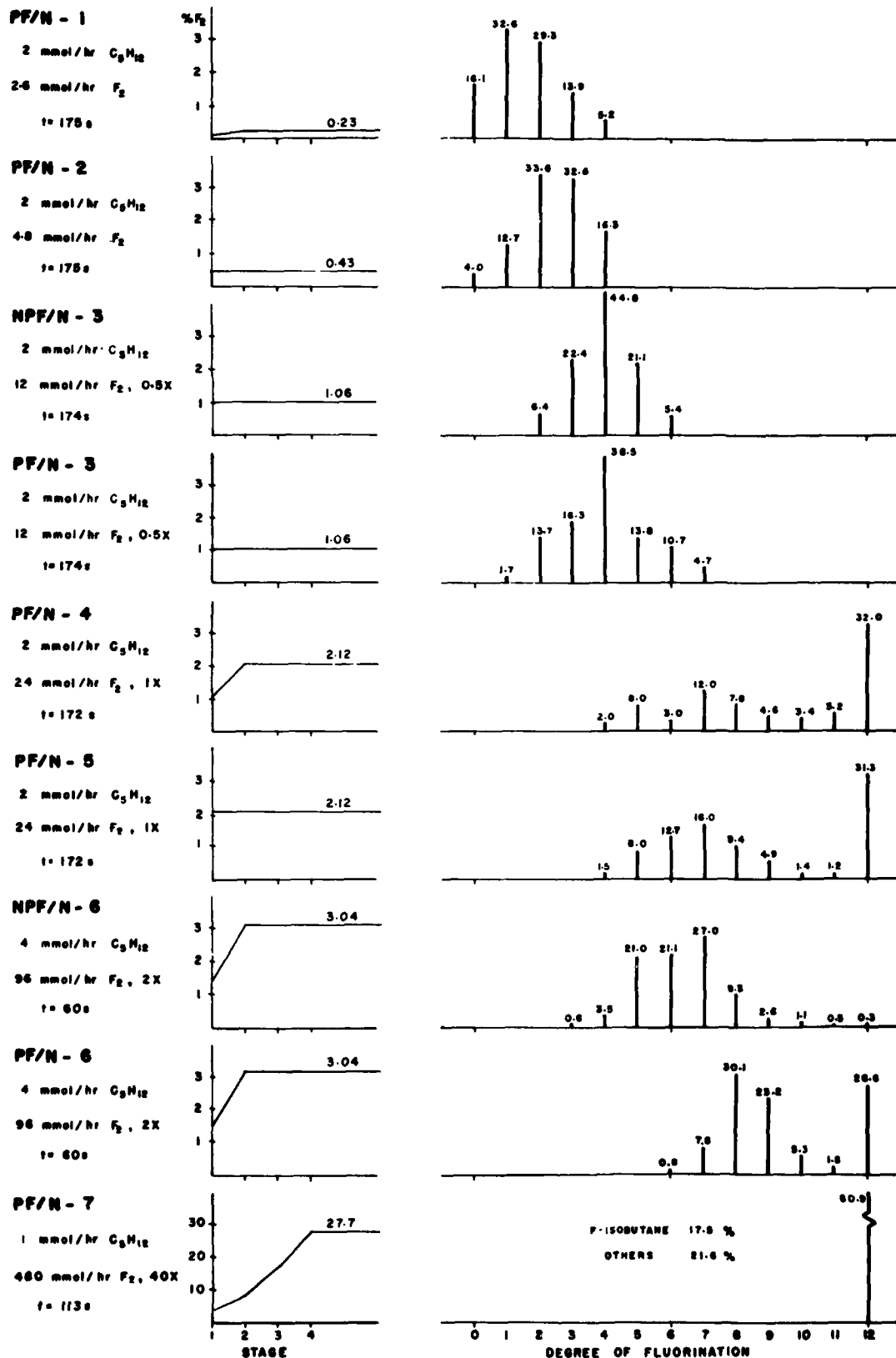


Figure 3. Neopentane photochemical product distributions.

Mass spectra of partially fluorinated 1,4-dioxanes are also very useful for identification; EI mass spectra usually show $C_2F_nH_{4-n}$ masses with very high intensities, from which the number of fluorine atoms on each side of the ring can be determined.^{30a,b} This information allowed the

product distribution graphs to be readily constructed for reactions producing the more highly fluorinated 1,4-dioxane which may be cleanly separated by single GLC injection (Figure 4). Reaction PF/D-1 produced 0.7963 g of *F*-1,4-dioxane for a 3 h, 2 mmol/h run. Theoretical

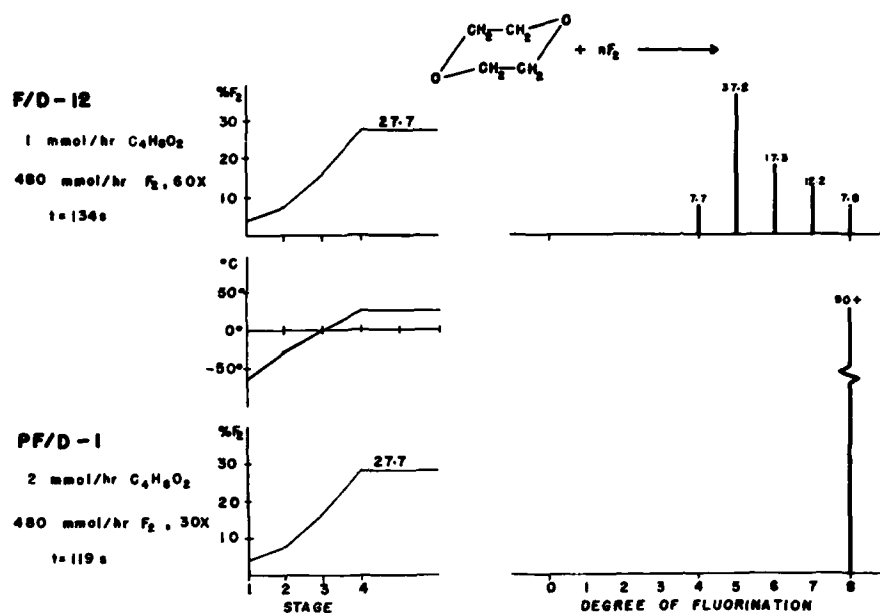


Figure 4. 1,4-Dioxane product distributions.

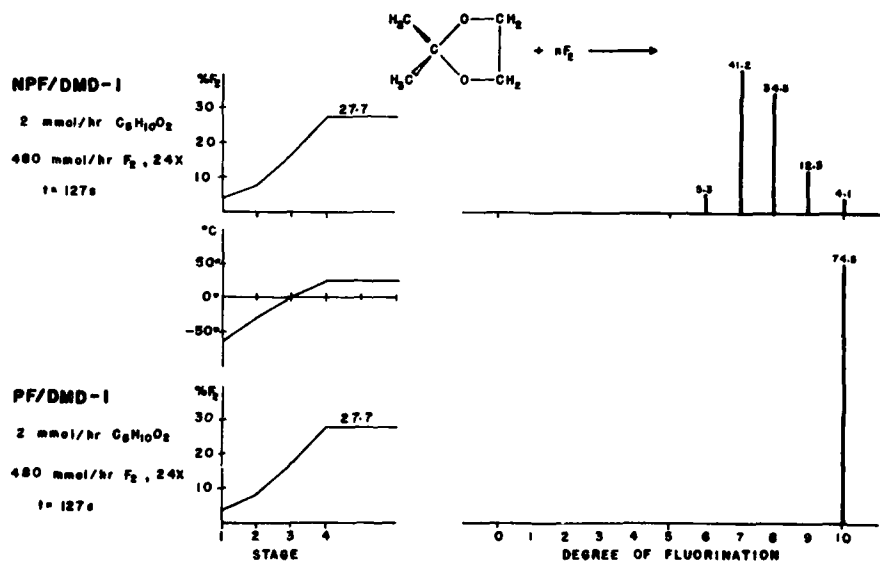


Figure 5. 2,2-Dimethyl-1,3-dioxolane product distributions.

Table V. Reaction Conditions for Photochemical Fluorinations of Neopentane, 2,4-Dioxane (PF/D), Cyclohexane (PF/C), and 2,2-Dimethyl-1,3-Dioxolane (PF/DMD) in the Four-Stage Aerosol Reactor

ref no.	hydro-carbon flow, mmol/h	hc carrier, ^a cm ³ /min	main carrier, cm ³ /min	F ₂ flows (cm ³ /min) in stage					F ₂ dil He flow, cm ³ /min
				1	2	3	4	Σ	
PF/N-7	1	101 ^a	400	20	20	60	100	200	4 × 5
PF/D-1	2	63 ^b	400	20	20	60	100	200	4 × 5
PF/C-1	2	29 ^c	400	20	20	60	100	200	4 × 5
PF/DMD-1	2	20 ^d	400	20	20	60	100	200	4 × 5

ref no.	temp (°C) of modules				hc:F ₂	stoichiometry in stage					% F ₂	reactn time, s
	reactor	no. 1	no. 2	coil		1	2	3	4	Σ		
PF/N-7	-65	-30	0	RT ^b	1:480	4	4	12	20	40	27.7	113
PF/D-1	-65	-30	0	RT	1:240	3	3	9	15	30	29.3	119
PF/C-1	-65	-30	0	RT	1:240	2	2	6	10	20	30.8	125
PF/DMD-1	-65	-30	0	RT	1:240	2.4	2.4	7.2	12	24	31.2	127

^a Hydrocarbon reservoir temp: (a) -78 °C, (b) 10 °C, (c) 0 °C, (d) 39 °C. ^b Room temperature.

yield estimate for 6 mmol of *F*-1,4-dioxane is 1.33 g, a yield of 57%.

Cyclohexane Reactions. Again many reactions at virtually all levels of fluorination were conducted with cyclohexane.³⁰ The highly complex ¹H and ¹⁹F NMR spectra due to extensive coupling and conformational equilibria have been to a great extent worked out in the literature.³³⁻³⁵ The difficulty in providing meaningful product distributions arises from the difficulties in obtaining quantitative separation of the various products which required use of up to three, generally two, different GLC columns on each complex fraction. For this reason only the photochemical results for conditions (Table V, PF/C-1) leading to perfluorination are reported in this work. The product collected was almost pure *F*-cyclohexane in 30% yield on the basis of average throughput of 2 mm/h.

2,2-Dimethyl-1,3-dioxolane Reactions. Only reaction conditions leading to a high degree of fluorination are tabulated (PF/DMD-1, Table V). Characterization of various hydryl-*F*-2,2,2-dimethyl-1,3-dioxolanes, are given in the literature.³⁶ The product distributions (Figure 5) represent only those seven major components (~70% total) which are "stable" to the NaF/L-4A treatment and do not pass a -131 °C trap at 10⁻³ torr. The product distributions (Figure 5) are estimates on the basis of gas chromatographic assay on fluorosilicone QF-1 using the temperature separation program *T*₁ = -8 °C for 8 min, heating 8 °C/min, and *T*₂ = 144 °C for 20 min. The photochemical fluorination resulted in collection of 1.1593 g of material at an average hydrocarbon throughput of 2 mmol/h for 3 h. GLC purification of the product gave 0.87 g (74.5%) of pure *F*-2,2-dimethyl-1,3-dioxolane, resulting in a yield estimate of 51.4%.

Results and Discussion

Neopentane, 1,4-dioxane, cyclohexane, and 2,2-dimethyl-1,3-dioxolane have all been successfully fluorinated by the aerosol process. Neopentane, however, was chosen as the model compound for detailed study of the reactor system for several reasons. The most important reasons are the following: all partially fluorinated neopentanes are stable, have a high volatility, and are soluble in CCl₄. There are fewer isomers and only one molecular conformation for each isomer. Gas chromatographic separation in one step has proved to be possible, so that the GLC-chromatogram could be used for quantitative estimation of product distributions. Therefore the influence of reaction parameters should be more easily seen directly from the product distribution. Also four of the most highly fluorinated neopentanes (i.e., *F*-neopentane, undecafluoroneopentane, decafluoroneopentanes, and nonafluoroneopentanes) are known from LTG fluorinations, thus making it easier to judge the "success" of a fluorination.^{14,37}

Initially 21 nonphotochemical reactions with neopentane were run and the results compared.³⁰ In each of these reactions variables such as carrier flow, fluorine concentration gradient, reaction time, and hydrocarbon mass throughput were changed. Repetitive runs were made, generally only one variable at a time was changed so as to ascertain its effect on product distributions. Examination of all data indicates that the most important variables affecting product distributions are fluorine concentration and reaction time. A comparison of F/N-7 (Figure 2) with NPF/N-3 (no UV control of PF/N-3, Figure 3) establishes this fact. A similar concentration of F₂, a 16:1 excess of fluorine, a 1:24 difference in reaction time give rise to a similar product distribution. A much more efficient use of fluorine. Multistaging accomplishes the expected goal of replenishing fluorine consumed and increasing fluorine concentrations gradually to compensate for increased inactivation of hydrocarbon due to increased fluorine substitution. Multistaging, addition of coils, and decrease of carrier flow all serve to increase reaction time. In none of these reactions was the reactor or reaction uncontrolled or perceptively violent even in those runs involving fluorine flows exceeding 200 cm³/min (480 mmol/h). The product distributions for typical neopentane fluorinations are given in Figure 2. In this diagram isomers are combined to

illustrate the degree of fluorination obtained as a function of fluorine concentration, concentration gradients (i.e., multistaging), relative F₂: hydrocarbon stoichiometry, and reaction time. It is quite evident that a Gaussian distribution of products is approached. This is seen most clearly in reactions F/N-1, F/N-11, F/N-17, and F/N-20. Significant deviations however occur for certain sets of conditions. The most readily explicable is that illustrated by F/N-21, Figure 2. In this reaction only the hydrocarbon throughput was increased (fourfold) relative to F/N-20. This effect, a compression of the maximum toward lower substitution, is probably due to fluorine concentration gradient changes as the increased hydrocarbon throughput consumes additional fluorine; however, mean aerosol particulate size effects could be partly responsible for the spread of products.

Preferential Fluorine Reactivity

The preceding discussion suggests that fluorination occurs stepwise under our conditions and that product distributions with regard to degree of fluorination should be readily explainable on simple statistical and kinetic grounds. The question which remains is whether each degree of fluorination exhibits a distribution of isomers on the basis of simple statistics. In this regard it became necessary to identify each possible isomer, its statistical weight on the basis of the assumption of stepwise fluorination, and the comparison of the theoretical with the experimental distribution of isomers (Table V). Because of the nature of the aerosol process, the assumption that only effects due to statistical weighting or internal directive effects should be important is a defensible one. The basic process involves finely dispersed hydrocarbon particulates in a gaseous helium matrix which are subjected to diffusion controlled attack by gaseous fluorine. Fluorine is injected evenly along the reactor length so as to produce a dynamic fluorine concentration gradient which is ideally at a steady state. Thus the fluorine concentration should remain constant at any given point along the reactor length. This unique set of conditions roughly approximates the conditions produced by a molecular beam apparatus where two reactants intersect and react in a manner governed by condition dependent statistical probability as operated on by the intrinsic reactivities of the reactants themselves. In the aerosol system the intersecting points are random, diffusion controlled, and compound permitting only statistical treatment and an approximate one at that. It should however be possible to achieve a qualitatively valid comparison between experiment and theory.

The statistical probability of isomers on the basis of the assumption of stepwise substitution are illustrated for neopentane (Figure 6). In each case the probability of the most symmetrical isomer is underlined. The experimentally determined isomer distribution (which is the average of three to five reactions) was determined by comparison of relative peak areas of the gas chromatographed products. In all cases the most unequivocal results are those where two or more isomers are isolated. However single isomer products may be considered at least fivefold probably tenfold larger than any nondetected, nonisolated isomers.

The results indicate that substitution is near statistical until one reaches the pentafluoroneopentane. At this point only the most symmetrical isomer is isolated. This would indicate that a hydrogen of a CH₃ group is more reactive than a hydrogen of a CH₂F or CHF₂ group. At the next step only one hexafluoroneopentane is isolated, indicating that a hydrogen on a CH₂F is more readily substituted than a CHF₂; however this is also statistically the predicted major isomer. The more definitive case comes at the heptafluoroneopentane where again the only isomer isolated is the most symmetrical. However here the unsymmetrical isomer (CF₃)C(CH₂F)₂(CHF₂) is of equal probability. This is a more convincing case for the greater reactivity of hydrogens on CH₂F relative to CHF₂. The octafluoroneopentane case also supports this contention. The theoretical distribution of the unsymmetrical isomer (CF₃)C(CHF₂)₂(CH₂F) to the symmetrical C(CHF₂)₄ is 4:1; however the experimental distribution is closer to 1:1. Again at the nonafluoroneopentane the lowered reactivity of the CHF₂ group is indicated in that the ratio of isomers

(33) J. Homer and L. F. Thomas, *Trans. Faraday Soc.*, **59**, 2431 (1963).
(34) F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.*, **40**, 3099 (1964).

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(36) R. D. Bagnall, W. Bell, and K. Pearson, *J. Fluorine Chem.*, **9**, 359 (1977).

(37) J. L. Adcock and E. B. Renk *J. Org. Chem.*, **44**, 3431 (1979).

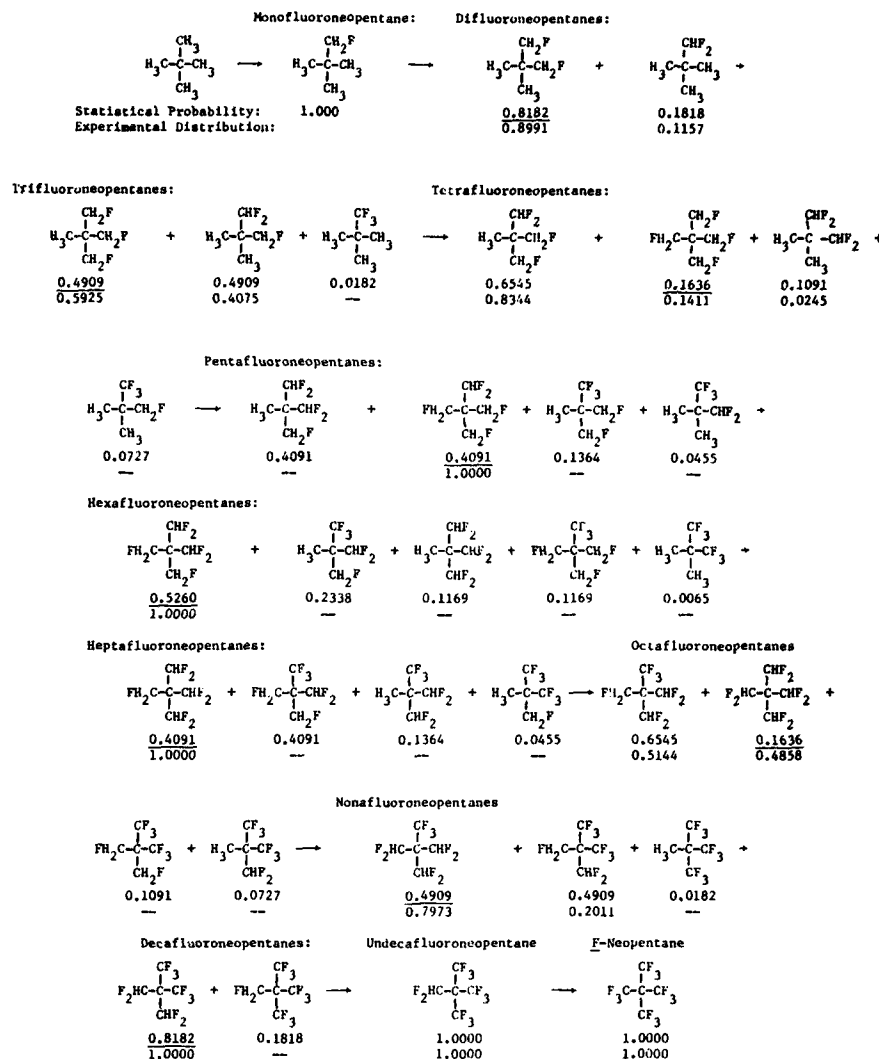


Figure 6. The Statistical probability of Isomers based on stepwise substitution of hydrogens by fluorine.

(CF₃)₂C(CHF₂)(CH₂F) to (CF₃)C(CHF₂)₃ theoretically is 1:1; however the experimental ratio is close to 1:4 with the symmetrical isomer predominating.

Although the experimental numbers themselves are of little theoretical value, the experimental isomer ratios compared to the theoretical isomer ratios indicate unequivocally that the reactivities of hydrogen atoms to attack by elemental fluorine can be altered and that hydrogens are not always indiscriminately attacked by fluorine in a purely statistical way. The apparent order of hydrogen reactivity is CH₃ > CH₂F > CHF₂ >> CF₃. This order not only parallels the order of steric accessibility of the hydrogen atoms but also parallels the expected order of electron density on the hydrogens. The latter effect if controlling would indicate that fluorine prefers the more electron-rich hydrogens. This at least suggests that selectivity in a molecule might be achieved by altering the electron density of the carbon bearing the hydrogen.

Photochemical Assisted Fluorinations

The addition of the photochemical reaction stage to the aerosol fluorinator allows the achievement of high degrees of perfluorination although at the expense of some fragmentation (PF/N-7, Figure 3). Yields are still quite high for those "expected" for an elemental fluorine reaction and certainly one utilizing photochemical activation in the final stages. The key to molecular integrity is obviously the fact that molecules entering the gradient photochemical cell are already highly fluorinated (cf. F/N-20 with PF/N-7, Figures 2 and 3) and are therefore more

robust and capable of resisting fragmentation under vigorous attack by both molecular and atomic fluorine. It is significant to note that the photochemical cell has not in nearly 1 year of use become befouled and to the contrary looks almost as good as the day it was initiated. A ultraviolet transmission spectrum of the 0.015-in. FEP Teflon film shows that its absorbance curve is near zero and flat until it shuts off at 224 nm in the ultraviolet. It is however of utmost importance to keep the polymer wall near 25 °C as it begins to lose its structural rigidity about 50 °C, forming kinks in the smooth coil. A word of caution is in order; since atomic fluorine is produced in the photochemical cell, excessive temperatures may cause the FEP Teflon to be attacked with disastrous results at the higher fluorine flows.

The higher fluorine flows produce "anomalous" results in the product distributions of the neopentane photochemical reactions. Unlike the "dark" reactions and PF/N-1 through PF/N-3 which give a successively higher degree of fluorination with increasing concentration, PF/N-4 begins to produce F-neopentane. The almost identical product distributions in NPF/N-3 (no UV control) and PF/N-3 indicate that in PF/N-1 through PF/N-3 virtually all of the fluorine is consumed by the dark reaction prior to exposure to the ultraviolet irradiation. This finding indicates that hydrocarbons are very reactive to elemental fluorine in the dark at low temperatures but that increasing fluorine substitution deactivates the molecules toward further attack, at least in the kinetic sense. Somewhere between half and complete fluorination

molecules become quite resistant to rapid fluorine attack.

A comparison of the control NPF/N-6 with PF/N-6 (Figure 3) indicates that although general upward movement in the product distribution toward higher fluorination occurs, "anomalous" production of *F*-neopentane also occurs. This "anomalous" production of *F*-neopentane in reactions PF/N-4-6 must be due to a "hot molecule" effect. That is, fluorinated neopentanes attacked by atomic fluorine in the photochemical stage become chemically excited and thus more reactive toward fluorine. These "hot molecules" react much more rapidly than nonexcited fluoroneopentanes.

The results seen in reaction PF/N-7 result from two main factors. Molecules are more highly fluorinated when they enter the photochemical stage (cf. F/N-20 (Figure 2) vs. PF/N-7 (Figure 3)), and the fluorine concentration is high enough to exceed the threshold for radical chain propagation throughout the reaction mixture. Both factors contribute toward perfluorination while molecular integrity is maintained to a high degree.

The fluorination of 1,4-dioxane dramatizes the effectiveness of the photochemical stage (Figure 4). The crude product collected from the reactor is better than 90% pure *F*-1,4-dioxane in yields approaching 60%. The extremely difficult direct fluorination of cyclohexane to perfluorocyclohexane can be accomplished in yields exceeding 30% and a product purity in excess of 90% direct from the reactor. The low yields are due to tar formation in stage one which we should be able to eliminate by reducing the fluorine concentration gradient at this stage.

Absence of Hydrogen Fluoride Solvolysis

The direct fluorination reaction produces a molecule of hydrogen fluoride for every hydrogen substituted. It was of interest to determine whether acid-catalyzed cleavage would occur in the reactor system to an appreciable extent. The very acid sensitive ketal, 2,2-dimethyl-1,3-dioxolane, was chosen for this determi-

nation. The results indicate that HF solvolysis of such groupings is not a problem. It was possible to produce fluoro analogues of the 1,3-dioxolane in very good yields with almost no evidence of HF solvolysis (Figure 5). The photochemical perfluorination went uneventfully and actually produced higher overall yields than the 1,4-dioxane. Whether this lack of solvolysis is general will, of course, require reaction of many different compounds possessing different functionalities.

Summary

The multistaged aerosol fluorination reactor achieves near optimum control over the potentially violent direct fluorination reaction. This system meets all of the criteria enumerated earlier which we, by experience, believe contribute to high yield direct fluorination reactions. It additionally has other distinct advantages in that the degree of fluorination may be controlled: it is a flow process, the process is not highly dependent on the physical properties of the reactant to be fluorinated, reactant throughputs may be varied over a considerable range for a given design, fluorine concentration and temperature conditions may be tailored to the reactivity of the reactant, and most importantly the observation of nonstatistical substitution effects suggests that this system might permit the elusive achievement of selectivity in direct fluorinations.

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Supplementary Material Available: Table A, IR, mass spectra, and elemental analyses for partially fluorinated neopentanes (7 pages). Ordering information is given on any current masthead page.

APPENDIX II

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