

AD-A139 195

AEROSOL DIRECT FLUORINATION: SYNTHESIS OF THE HIGHLY
BRANCHED KETONES F-P..(U) TENNESSEE UNIV KNOXVILLE DEPT
OF CHEMISTRY J L ADCOCK ET AL. 31 JAN 83 TR-10

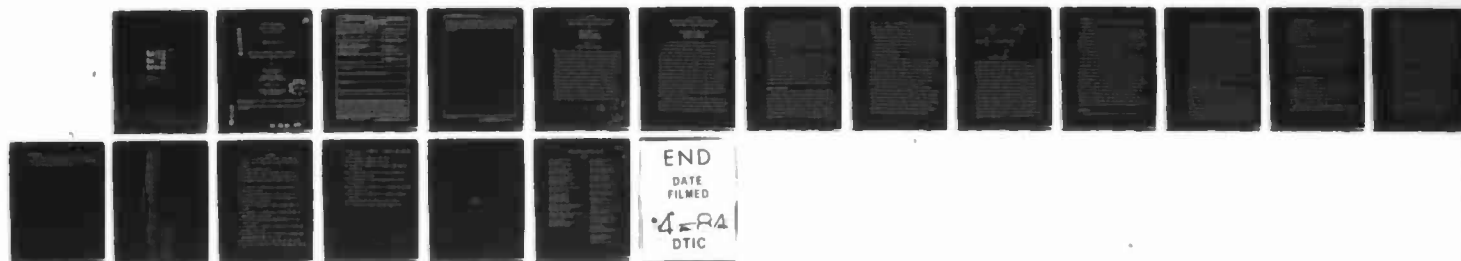
1/1

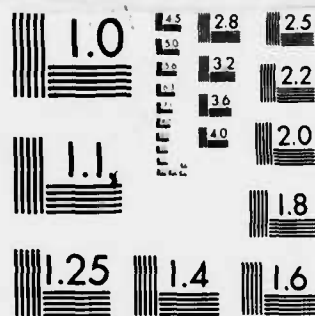
UNCLASSIFIED

N00014-77-C-0685

F/G 7/4

NL





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

12

OFFICE OF NAVAL RESEARCH

Contract No. N00014-77-C-0685

Task No. NR 053-669

TECHNICAL Report No. 10

AD A139195

AEROSOL DIRECT FLUORINATION: SYNTHESSES OF THE HIGHLY
BRANCHED KETONES, F-PINACOLONE and "F-PROVALONE"

by

James L. Adcock* and
Mark L. Robin

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

January 31, 1983

Prepared for Publication in the
Journal of Organic Chemistry
MS 3-307C REVISED

DTIC
SELECTED
MAR 21 1984
S A

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

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

DTIC FILE COPY

84 03 20 004

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No 10	2. GOVT ACCESSION NO. AP-A139195	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Low Temperature Fluorination of Aerosol Suspensions of Hydrocarbons Utilizing Elemental Fluorine-"Aerosol Direct Fluorination: Syntheses of the Highly Branched Ketones, F-Pinacolone and 'F-Provalone'"		5. TYPE OF REPORT & PERIOD COVERED Interim
7. AUTHOR(s) James L. Adcock and Mark L. Robin		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Tennessee-Knoxville Knoxville, Tennessee 37996-1600		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0685
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-669
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE January 31, 1984
		13. NUMBER OF PAGES 17
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Aerosol, Direct Fluorination, Elemental Fluorine, Ketones, Perfluoroketones		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The extension of aerosol direct fluorination techniques to the syntheses of the here-to fore unknown highly branched perfluoroketones F-3,3-dimethyl-2-butanone (F-pinacolone) and F-2,2,5-trimethyl-3-hexanone ("F-provalone") from 3,3-dimethyl-2-butanone (pinacolone) and 2,2,4,4-tetramethyl-3-pentanone (pivalone) respectively demonstrates again the efficacy of the aerosol direct fluorination process for the synthesis of perfluoroketones directly from ketones. The interesting rearrangement of the hydrocarbon di-tert-butyl ketone (pivalone) to the perfluorinated tert-butyl iso-butyl ketone, "F-provalone" is unprecedented in our experience		

DD FORM 1 JAN 73 1473

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

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

and does not occur at the monofluorination step but later in the fluorination. Isolated yields of 12% and 9% though modest are unadjusted by physical losses of recoverable hydrocarbons present at the termination of the reaction. Perfluorinated product distributions, concentrations of products collected from the reactor effluent, are 23% and 71% of the total material traversing the reactor.

S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

MS 3-307C REVISED

AEROSOL DIRECT FLUORINATION: SYNTHESSES OF THE HIGHLY
BRANCHED KETONES, F-PINACOLONE AND "F-PROVALONE"

by

James L. Adcock* and
Mark L. Robin
Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600

Submitted to

Journal of Organic Chemistry

The extension of aerosol direct fluorination techniques to the syntheses of the here-to-fore unknown highly branched perfluoroketones F-3,3-dimethyl-2-butanone (F-pinacolone) and F-2,2,5-trimethyl-3-hexanone (F-provalone) from 3,3-dimethyl-2-butanone (pinacolone) and 2,2,4,4-tetramethyl-3-pentanone (pivalone) respectively demonstrates again the efficacy of the aerosol direct fluorination process for the synthesis of perfluoroketones directly from ketones. The interesting rearrangement of the hydrocarbon di-tert-butyl ketone (pivalone) to the perfluorinated tert-butyl iso-butyl ketone, F-provalone is unprecedented in our experience and does not occur at the monofluorination step but later in the fluorination. Isolated yields of 12% and 9% though modest are unadjusted by physical losses of recoverable hydrocarbons present at the termination of the reaction. Perfluorinated product distributions, concentrations of products collected from the reactor effluent, are 23% and 71% of the total material traversing the reactor.



Attention For	
MR. GRAAL	☒
MR. TAB	☐
Unannounced	☐
Postmark	
Distribution/	
Availability Codes	
Avail and/or	
Special	
A-1	

Aerosol Direct Fluorination: Syntheses of the Highly
Branched Ketones, F-Pinacolone and F-Provalone

by

James L. Adcock and Mark L. Robin
Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600

The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation. The application of this process to alkanes, ethers, cycloalkanes, and ketals has been demonstrated.¹ Extension of this novel process to ketones has provided direct access to analog perfluoroketones in modest yields, and has led to the successful perfluorination of methyl ketones² as well as both symmetric and unsymmetric long chain ketones.³ Aerosol direct fluorination of the cycloalkyl methyl ethers or cycloalkyl ethylene glycol ketals have produced the corresponding perfluorinated analogs, which can be converted in good yields to the corresponding perfluorocycloketones via treatment with 100% sulfuric acid.⁴ We report here the aerosol direct fluorination of the highly branched ketones 3,3-dimethyl-2-butanone (pinacolone) and 2,2,4,4-tetramethyl-3-pentanone (pivalone); aerosol direct fluorination of 2,2,4,4-tetramethyl-3-pentanone results in the first example of a skeletal rearrangement occurring during the aerosol fluorination of ketones.

In general, routes to perfluoroketones, other than the aerosol direct fluorination process, require either the prior preparation of highly chlorinated species, or (in most cases) highly fluorinated species. The Swarts reaction and other reactions involving halogen exchange require preparation

of the corresponding chlorocarbons prior to fluorination, and the higher perchlorocarbons are often difficult to prepare. Typical preparations of perfluoro ketones include the decomposition over Lewis acid catalysts of perfluoroalkylene epoxides⁶⁻¹³ and the reaction of perfluoroalkyl carboxylates or perfluoroacyl chlorides with organometallic reagents such as perfluoropropyl lithium, perfluoropropyl magnesium iodide, or perfluoropropyl zinc iodide.¹⁴⁻¹⁸ In contrast to the above, the aerosol direct fluorination method has provided direct access to perfluoroketones from the relatively inexpensive hydrocarbon analogs.³

Whereas a number of straight chain perfluoro ketones are known, relatively few branched perfluoroketones are known. The fluoride ion catalyzed addition of perfluoroacyl fluorides to F-propene affords a route to perfluoro ketones containing the branched perfluoroisopropyl group,¹⁹⁻²³ and these represent the majority of the known branched perfluoroketones. Only two other branched perfluoroketones have been reported in the literature: F-4-methyl-2-pentanone, formed via the Lewis acid catalyzed opening of F-3-methyl-2-butenyl epoxide¹⁰ and F-4-methyl-2-heptanone, formed via the treatment of F-2-chlorosulfato-4-methylheptane with potassium fluoride.²⁴

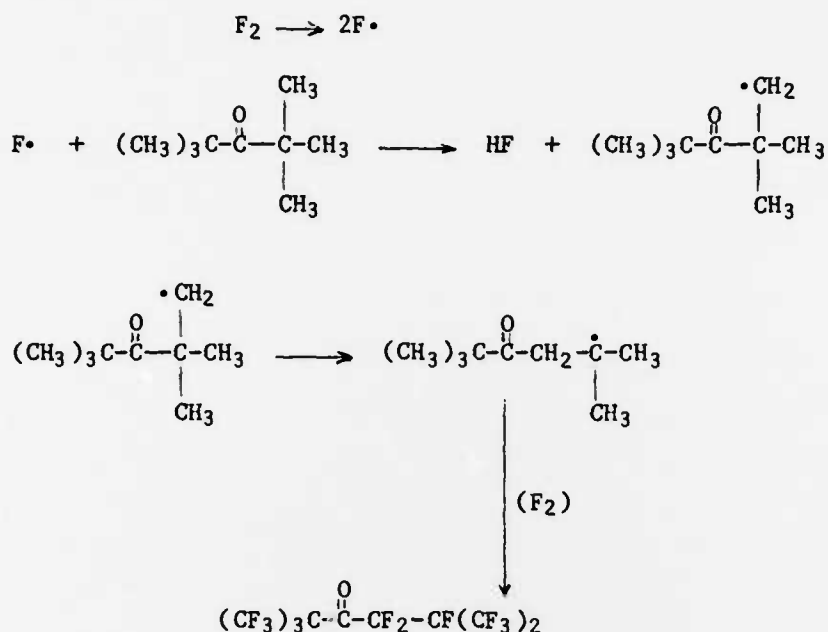
Results and Discussion

The aerosol direct fluorination of 3,3-dimethyl-2-butanone produced F-3,3-dimethyl-2-butanone, 3-difluoromethyl-F-methyl-2-butanone and 3,3-bis-(difluoromethyl)-F-2-butanone as the major products, constituting 23%, 25%, and 12% of the total products collected by weight, respectively. The aerosol system is dependent on the generation of a particulate aerosol that is ideally crystalline, monodisperse, and with little tendency to aggregate. If the conditions considered ideal are met, percent yields based on throughput (amounts injected) and product (collected) percent distributions will differ

by only a few percent. As deviations from this ideality occur, the percent yields based on throughput begin to fall due to physical losses within the aerosol generator and initial reaction stage (see ref 1). These losses can be significant and result in sometimes significant amounts of unfluorinated or complex mixtures of generally less than trifluorinated products collected at the close of the reactions when the system warms to ambient or is opened for cleaning between reaction runs. Although significant advances in optimization have been made, this is as much art as science. If no corrections are made due to recovered unreacted or partially reacted materials, the yield of F-3,3-dimethyl-2-butanone was 12%.

The isolation of significant quantities of the mono- and di-hydril products reflects the sterically crowded nature of the fluorinated tert-butyl group; wherein replacement of the final hydrogens becomes increasingly difficult due to increased fluorine shielding of the residual hydrogens of the fluorinated tert-butyl group. It should be noted that in the aerosol direct fluorination of straight chain ketones the major product in all cases is the perfluorinated product; mono- and di-hydril products typically amount to no more than a few percent of the total products collected.^{2,3}

Aerosol direct fluorination of 2,2,4,4-tetramethyl-3-pentanone (pivalone) produced F-2,2,5-trimethyl-3-hexanone ("F-provalone") as the major product. This result represents the first example of a skeletal rearrangement occurring during the aerosol fluorination of ketones. Since the first step in the direct fluorination process involves the abstraction of hydrogen, it was originally proposed that this novel rearrangement involved a rearrangement of the initially formed primary radical to the more stable tertiary radical, followed by fluorination in the usual fashion:



Subsequent experiments with a low concentration of fluorine (1:2 molar ratio of hydrocarbon to fluorine) showed however that the rearrangement must occur sometime after the first fluorine is added; the major product in these low fluorine runs (besides unreacted 2,2,4,4-tetramethyl-3-pentanone) is 1-fluoro-2,2,4,4-tetramethyl-3-pentanone, resulting from the simple replacement of hydrogen by fluorine and involving no rearrangement. The possibility of photolytic rearrangement of the starting material in the ultraviolet stage of the aerosol fluorination apparatus was also eliminated; reactions at low fluorine concentration both in the dark and with the operating ultraviolet stage produce 1-fluoro-2,2,4,4-tetramethyl-3-pentanone as the major product. The possibility of thermal rearrangement of the starting material in the flash evaporator/sublimator unit of the aerosol fluorination apparatus was also eliminated by subsequent experiments. For all the reactions at low fluorine concentrations only very small amounts of other fluorinated materials were present, but difficulty in separation and minimal quantities prevented their characterization. It would appear then that this

rearrangement occurs sometime after the introduction of the first fluorine. The elucidation of the mechanism of this novel rearrangement should prove to be interesting.

For a typical run at high fluorine concentrations, F-2,2,5-trimethyl-3-hexanone constituted 71% of the total products collected by weight, without correcting for unreacted or partially reacted materials the percent yield based on the amount of 2,2,4,4-tetramethyl-3-pentanone injected was 9%. The majority of losses are due to physical losses within the reactor as evidenced by the finding of unreacted 2,2,4,4-tetramethyl-3-pentanone inside the reactor upon opening of the system for cleaning.

The ^{19}F nmr spectrum of F-2,2,5-trimethyl-3-hexanone (see expt. section) consists of four multiplets of relative intensity 9:6:2:1 at $\delta = -61.61$, -71.82 , -109.32 , and -184.26 ppm (1% $\text{CFCl}_3/\text{CDCl}_3$ internal standard), corresponding to the tert-butyl CF_3 groups, the remaining CF_3 groups, the CF_2 group, and the methine fluorine, respectively. The CF_2 group appears as a hexadectet of doublets at $\delta = -109.32$ ppm due to coupling with all CF_3 groups and the methine fluorine. The hexadectet arises from the fact that the coupling constants of the CF_2 group with the two different type CF_3 groups are identical. Further confirmation of the structure is supplied by the mass spectrum. The chemical ionization mass spectrum includes intense peaks at $m/e = 483$, 467 , and 447 corresponding to the molecular ion plus CH_5 , the molecular ion plus hydrogen, and the molecular ion minus fluorine, respectively, in addition to a base peak at $m/e = 219$ due to the C_4F_9^+ fragment. The electron impact mass spectrum exhibits a peak at $m/e = 447$ due to the molecular ion minus fluorine and a consistent fragmentation pattern.

Experimental

The basic aerosol fluorinator design and a basic description of the

The basic aerosol fluorinator design and a basic description of the process is presented elsewhere.¹ A modified aerosol generator adapted to a flash evaporator fed by a syringe pump driving a 5 mL Precision Sampling Corp "Pressure Lok" Syringe was employed for the reactions.²⁵ Workup of products following removal of hydrogen fluoride consisted of vacuum line fractionation, infrared assay of fractions, gas chromatographic separation of components using either a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh, acid washed Chromosorb P conditioned at 225°C (12 h) or a 4 meter x 3/8" 10% SE-52 phenyl-methyl silicone rubber on acid washed 60-80 mesh Chromosorb P, conditioned at 250°C (12 h). Following gas chromatographic separation (Bendix model 2300, subambient multicontroller) all products of significance were collected, transferred to the vacuum line, assayed and characterized by vapor phase infrared spectrophotometry (PE 1330), electron impact (70 eV) and chemical ionization (CH₄ plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980A MS, 5934A computer) and ¹H and ¹⁹F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in CDCl₃ with 1% CFCl₃ internal standard. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Aerosol Fluorination of 3,3-dimethyl-2-butanone. 3,3-Dimethyl-2-butanone (Aldrich) was used as received. A pump speed corresponding to 2.8 mmol/h was established and 0.8 mL 3,3-dimethyl-2-butanone was delivered over a 2.25 h period. Details of the aerosol fluorination parameters are given in Table 1. From the crude product was isolated 0.238 g (23%) F-3,3-dimethyl-2-butanone, 0.258 g (25%) 3-difluoromethyl-F-3-methyl-2-butanone, and 0.134 g (13%) 3,3-bis(difluoromethyl)-F-2-butanone (GLC temperature program on the QF-1 column; 0°C, 2 m; 1°C/m to 10°C; 10°C, 1 m; 20°C/m to 180°C). The yield of F-3,3-dimethyl-2-butanone based on 3,3-dimethyl-2-butanone injected was 12%. The characterization of these new compounds are given below.

F-3,3-Dimethyl-2-butanone. $\text{CF}_3^{\text{A}}\text{C}(\text{O})\text{C}(\text{CF}_3^{\text{B}})_3$: IR (cm^{-1}) 1770 (m), 1275 (vs), 1230 (s), 1200 (s), 1055 (w), 985 (m), 870 (m), 730 (m), 720 (m), 690 (w). Major mass cations were [m/e(int.)formula]: [CI] 317(59) $\text{C}_6\text{F}_{12}\text{OH}$, M+H; 297(84) $\text{C}_6\text{F}_{11}\text{O}$, M-F; 97(100) $\text{C}_2\text{F}_3\text{O}$; 69(58) CF_3 : [EI] 181(16) C_4F_7 ; 97(21) $\text{C}_2\text{F}_3\text{O}$; 69(100) CF_3 . ^{19}F NMR [1% $\text{CFCl}_3/\text{CDCl}_3$] $\delta_{\text{A}} = -73.88$ ppm (d), $\delta_{\text{B}} = -61.12$ ppm (q), $J_{\text{AB}} = 6.1$ Hz. Anal. Calcd for $\text{C}_6\text{F}_{12}\text{O}$: C, 22.80; F, 72.13. Found: C, 21.37; F, 72.43.

3-Difluoromethyl-F-3-methyl-2-butanone. $\text{CF}_3^{\text{A}}\text{C}(\text{O})(\text{CF}_2^{\text{B}}\text{H}^{\text{C}})(\text{CF}_3^{\text{D}})_2$: IR (cm^{-1}) 3015 (w), 1760 (m), 1390 (m), 1370 (m), 1275 (vs), 1235 (vs), 1190 (s), 1135 (m), 1120 (m), 1065 (m), 1020 (w), 980 (s), 910 (w), 870 (s), 765 (m), 750 (m), 730 (s), 705 (m), 655 (m). Major mass cations were [m/e(int.)formula]: [CI] 300(8) $\text{C}_6\text{F}_{11}\text{OH}_3$, M+2H; 164(100) $\text{C}_4\text{F}_6\text{H}_2$; 97(15) $\text{C}_2\text{F}_3\text{O}$: [EI] 231(28) C_5F_9 ; 164(33) $\text{C}_4\text{F}_6\text{H}_2$; 160(61) $\text{C}_4\text{F}_5\text{OH}$; 97(50) $\text{C}_2\text{F}_3\text{O}$; 69(100) CF_3 ; 51(38) CF_2H . ^{19}F NMR [1% $\text{CFCl}_3/\text{CDCl}_3$] $\delta_{\text{A}} = -73.85$ ppm (m), $\delta_{\text{B}} = -126.69$ ppm (m), $\delta_{\text{D}} = -62.05$ ppm (m). ^1H NMR $\delta_{\text{C}} = +6.63$ ppm (t); $J_{\text{CF}_2\text{H}} = 51.5$ Hz.

3,3-Bis(difluoromethyl)-F-2-butanone. $\text{CF}_3^{\text{A}}\text{C}(\text{O})(\text{CF}_3^{\text{B}})(\text{CF}_2^{\text{C}}\text{H}^{\text{D}})_2$: IR (cm^{-1}) 3010 (w), 1755 (m), 1365 (w), 1275 (w), 1250 (vs), 1225 (vs), 1190 (s), 1160 (m), 1130 (m), 1060 (m), 1020 (m), 900 (w), 870 (w), 730 (s). Major mass cations were [m/e(int.)formula]: [CI] 282(100) $\text{C}_6\text{F}_{10}\text{OH}_4$, M+2H; 212(36) $\text{C}_5\text{F}_7\text{OH}_3$; 97(65) $\text{C}_2\text{F}_3\text{O}$; 69(43) CF_3 ; [EI] 212(64) $\text{C}_5\text{F}_7\text{OH}_3$; 146(41) $\text{C}_6\text{F}_3\text{OH}$; 142(100) $\text{C}_4\text{F}_4\text{OH}_2$; 97(35) $\text{C}_2\text{F}_3\text{O}$; 69(85) CF_3 ; 51(43) CF_2H . ^{19}F NMR [1% $\text{CFCl}_3/\text{CDCl}_3$] $\delta_{\text{A}} = -74.61$ ppm (m), $\delta_{\text{B}} = -62.99$ ppm (m), $\delta_{\text{C}} = -125.18$ ppm (m). ^1H NMR $\delta_{\text{D}} = +6.59$ ppm (t); $J_{\text{CF}_2\text{H}} = 52.7$ Hz.

Aerosol Fluorination of 2,2,4,4-Tetramethyl-3-pentanone. 2,2,4,4-Tetramethyl-3-pentanone (99%, Fluka Chemicals) was used as received. A pump speed

corresponding to 2.9 mmol/h was established and 1.0 mL 2,2,4,4-tetramethyl-3-pentanone delivered over a 2 hour period. Details of the aerosol fluorination parameters are given in Table 1. From the crude product (0.346 g) was isolated 0.246 g (71%) F-2,2,5-trimethyl-3-hexanone (GLC temperature program on the SE-52 gas chromatographic column: 30°C, 5 m; 5°C/m to 100°C; 100°C, 1 m; 20°C/m to 180°C). The yield of F-2,2,5-trimethyl-3-hexanone based on the amount of 2,2,4,4-tetramethyl-3-pentanone injected was 9%. Upon opening up the reactor for cleaning, significant amounts of unreacted 2,2,4,4-tetramethyl-3-pentanone were found. Runs with low fluorine concentrations (ultra-violet stage on or off) produced 1-fluoro-2,2,4,4-tetramethyl-3-pentanone as the major product. Characterizations of these compounds are given below.

F-2-2,5-Trimethyl-3-hexanone. $(\text{CF}_3^A)_3\text{CC}(\text{O})\text{CF}_2^B\text{CF}^C(\text{CF}_3^D)_2$: IR (cm^{-1}) 1770 (m), 1270 (vs), 1205 (m), 1150 (m), 1140 (m), 1045 (m), 980 (s), 730 (s), 710 (m), 680 (m). Major mass cations were $[\text{m/e}(\text{int.})\text{formula}]$: [CI] 483(2) $\text{C}_{10}\text{F}_{18}\text{OH}_5$, M+CH₅; 467(12) $\text{C}_9\text{F}_{18}\text{OH}$, M+H; 447(54) $\text{C}_9\text{F}_{17}\text{O}$, M-F; 247(55) $\text{C}_5\text{F}_9\text{O}$; 219(100) C_4F_9 ; 201(84) C_4F_8 ; 181(98) C_4F_7 ; 69(75) CF_3 : [EI] 447(1) $\text{C}_9\text{F}_{17}\text{O}$, M-F; 247(37) $\text{C}_5\text{F}_9\text{O}$; 219(43) C_4F_9 ; 69(100) CF_3 . ^{19}F NMR (1% $\text{CFCl}_3/\text{CDCl}_3$) $\delta_A = -61.61$ ppm (t of m), $\delta_B = -109.32$ ppm (hexadec of doublets), $\delta_C = -184.26$ ppm (m), $\delta_D = -71.82$ ppm (t of d); $J_{AB} = J_{BD} = 10.26$ Hz, $J_{AD} = 0.88$ Hz, $J_{AC} = 0$, $J_{BC} = 4.40$ Hz, $J_{CD} = 6.10$ Hz. Anal. Calcd for $\text{C}_9\text{F}_{18}\text{O}$: C, 23.19; F, 73.37. Found: C, 22.33; F, 71.16.

1-Fluoro-2-2,4,4-tetramethyl-3-pentanone. $(\text{CH}_3^A)_3\text{CC}(\text{O})(\text{CH}_2^B\text{F}^C)(\text{CH}_3^D)_2$: IR (cm^{-1}) 2980 (m), 2950 (s), 2900 (m), 2870 (m), 1680 (s), 1475 (s), 1360 (s), 1290 (s), 970 (s). Major mass cations were $[\text{m/e}(\text{int.})\text{formula}]$: [CI] 161(4) $\text{C}_9\text{H}_{18}\text{OF}$, M+H; 103(28) $\text{C}_5\text{H}_8\text{OF}$; 101(46) $\text{C}_5\text{H}_6\text{OF}$; 59(100) C_2FO : [EI] 69(30) C_5H_9 ; 57(23) C_4H_9 ; 44(71) $\text{C}_2\text{H}_4\text{O}$; 32(100) CH_2F . ^{19}F NMR (1% $\text{CFCl}_3/\text{CDCl}_3/.2\% \text{CHCl}_3$) $\delta_C = -221.76$ ppm (t); ^1H NMR $\delta_A = +1.24$ ppm (s), $\delta_B = +4.40$ ppm (d), $\delta_D = +1.29$ ppm (s); $J_{\text{CH}_2\text{F}} = 47.4$ Hz.

Acknowledgement

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

TABLE I
TYPICAL AEROSOL FLUORINATION REACTION PARAMETERS^a

Starting Compound	Fluorine Flow ml/m Reactor Mod. 1 Mod. 2	Helium Diluent ml/m Reactor Mod. 1 Mod. 2	Reaction Temp. °C Reactor Mod. 1 Mod. 2	Main Helium Carrier ml/m	Hydrocarbon Throughput millimoles/hr (H.C. carrier)	Overall ^b Stoichiometry he:F ₂	Percent F ₂ Conc. Final Stage	Reac- tion Time ^c Sec. %	Product Distribution % Collected	Product Yield % Theoret- ical
3,3-Dimethyl-2-butanone	10 20 30	150 150 150	-40° -30° 10°	600	2.8 ^e	1:52	3.6%	49	23%	12%
2,2,4,4-Tetramethyl-3-pentanone	20 20 40	150 150 150	-30° -20° 10°	600	2.9 ^e	1:67	4.8%	49	71%	9% ^d

^aSee references 1 and 25 for the significance of these parameters.

^bOne milliliter/minute F₂ delivers 2.44 mmol/h F₂.

^cReactor volume/total flows; reactor volume = 1355 cc.

^dProduct is F-2,2,5-Trimethyl-3-hexanone.

^eTotal carrier flow through evaporator 550 ml/m (500 ml/m Primary, 50 ml/m secondary).

References

- (1) (a) J. L. Adcock, K. Horita and E. B. Renk, J. Amer. Chem. Soc., 1981, 103, 6937. (b) J. L. Adcock and E. B. Renk, U.S. Patent 4,330,475 (1982).
- (2) M. L. Robin, unpublished results.
- (3) J. L. Adcock and M. L. Robin, J. Org. Chem., 1983, 48, 2437.
- (4) J. L. Adcock and M. L. Robin, J. Org. Chem., 1984, 49, March.
- (5) R. D. Chambers, "Fluorine in Organic Chemistry," Wiley, N.Y., 1973, p. 16.
- (6) E. P. Moore and A. S. Milian (to E. I. du Pont de Nemours and Co.) U.S. Patent 3,321,515 (1967).
- (7) E. I. du Pont de Nemours and Co., Fr. Patent 1,416,013 (1965).
- (8) E. P. Moore and A. S. Milian (to E. I. du Pont de Nemours and Co.) British Patent 1,019,788 (1966).
- (9) P. L. Coe, J. H. Sleigh and J. C. Tatlow, J. Fluorine Chem., 1980, 15, 339.
- (10) A. Y. Zapevalov, T. A. Filyakova and I. P. Kolenko, Isz. Akad. Nauk SSSR, Ser. Khim., 1979, 12, 2812.
- (11) D. E. Morin (to Minnesota Mining and Manufacturing Co.) U.S. Patent 3,213,134 (1965).
- (12) A. Y. Zapevalov, I. P. Kolenko, V. S. Plashkin and P. G. Neifeld, Zh. Org. Khim., 1978, 14, 259.
- (13) S. A. Postovoi, E. I. Mysov, Yu. V. Zeifman and I. L. Knunyants, Isz. Akad. Nauk SSSR, Ser. Khim., 1982, 7, 1586.
- (14) A. L. Henne and W. C. Francis, J. Amer. Chem. Soc., 1953, 75, 992.
- (15) O. R. Pierce, E. T. McBee and G. F. Judd, J. Amer. Chem. Soc., 1954, 76, 474.

- (16) W. T. Miller, Jr., E. Bergman and A. H. Fainberg, J. Amer. Chem. Soc., 1957, 79, 4159.
- (17) R. N. Haszeldine, J. Chem. Soc., 1953, 1748.
- (18) R. N. Haszeldine, J. Chem. Soc., 1953, 1273.
- (19) R. D. Smith, F. S. Fawcett and D. D. Coffmann, J. Amer. Chem. Soc., 1962, 84, 4285.
- (20) F. S. Fawcett and R. D. Smith (to E. I. du Pont de Nemours and Co.) U.S. Patent 3,185,734 (1965).
- (21) F. S. Fawcett (to E. I. du Pont de Nemours and Co.) U.S. Patent 3,113,967 (1963).
- (22) Y. M. Vilencik, G. I. Lekontseva and L. S. Semerikova, Zh. Vses. Khim. o-Va., 1981, 26, 210.
- (23) R. D. Chambers, C. A. Heaton and W. K. R. Musgrave, J. Chem. Soc. C., 1968, 1933.
- (24) Pennsalt Chemicals Corp., British Patent 926,411 (1963).
- (25) J. L. Adcock and M. L. Robin, J. Org. Chem., 1983, 48, 3128.

APPENDIX I
Distribution List

TECHNICAL REPORT DISTRIBUTION LIST. GEN

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

ATE
LME