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AEROSOL DIRECT FLUORINATION: ORTHOESTERS, SYNTHESIS OF PERFLUOROMETHYLOR-
THOCARBONATE AND PERFLUOROETHYLENE ORTHOCARBONATE

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SUMMARY

The extension of aerosol direct fluorination techniques to orthoesters is described. Perfluorinated orthocarbonates can be isolated in modest yield from the direct fluorination of the analogous hydrocarbon orthocarbonates. They are stable, relatively unreactive and highly volatile. From the aerosol fluorination of tetramethyl orthocarbonate perfluorotetramethyl orthocarbonate (8%) and perfluorotrimethyl orthoformate (19%) can be isolated. The fluorination of ethylene orthocarbonate produces perfluoroethylene orthocarbonate (17%) and a small amount of a second product presumed to be perfluoroethylene carbonate. The fluorination of trimethyl orthoacetate resulted in the isolation of perfluoro-1,1-dimethoxyethane (24%). All starting materials undergo extensive beta scission during fluorination a result of alkoxy stabilized radicals.

INTRODUCTION

The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation [1-3]. The application of this process to

alkanes, cycloalkanes, alkyl chlorides, ethers, esters, ketals, and ketones has been demonstrated [1-11]. The extension of this novel process to orthocarbonates provides direct access to analog perfluoroalkyl orthocarbonates, a feat not realized by other available fluorination methods. We report here the first syntheses of perfluorotetramethyl orthocarbonate and perfluoroethylene orthocarbonate which are obtained in modest yields via the aerosol direct fluorination of the corresponding hydrocarbons.

Hydrocarbon orthocarbonates are typically prepared by the action of sodium alkoxides on trichloronitromethane (chloropicrin) [12]. While fluorinated alkoxides are known, difficulties arise in their use in synthesis due to the fact that the perfluorinated alkoxides are very weak nucleophiles; are highly dissociated or undergo competing side reactions at the temperatures necessary for reaction [13]. A small number of trihydyl perfluoroalkyl orthocarbonates, $(R_fCH_2O)_4C$, where $R_f = H(CF_2)_n$ ($n = 2,4,6$) have been synthesized via the reaction of the corresponding fluorinated alcohols with carbon tetrachloride in the presence of a ferric chloride catalyst. These trihydyl perfluoroalkyl orthocarbonates have found use as hydraulic fluids, heat-exchange fluids, lubricants, and dielectric fluids [14, 15]. The perfluoroalkyl orthocarbonates are not accessible via this route however. Perfluorinated alcohols R_fCF_2OH are not available, due to the instability of $-CF_2OH$ to loss of hydrogen fluoride [16].

Orthoesters are acid sensitive and like ketals can be fluorinated without decomposition only under low acidity conditions such as those which prevail in the aerosol direct fluorination system. This precludes the synthesis of perfluorinated orthoesters by the usual fluorination methods.

The related compounds, the perfluoroalkyl orthothiocarbonates, $(R_fS)_4C$, are available via the reaction of a perfluoroalkylthio metal compound with tetrabromomethane, and have found use as solvents for difficultly soluble polymers such as low molecular weight tetrafluoroethylene polymer [17, 18].

EXPERIMENTAL

The basic aerosol fluorinator design and a description of the process are presented elsewhere [1, 2]. A modified aerosol generator, adapted to an evaporator/sublimator unit, was employed in the reactions [11]. Details of the aerosol fluorination parameters are given in Table 1. Tetramethyl orthocarbonate was fed into the evaporator/sublimator unit via a 5 mL Precision Sampling Corp, "Pressure Lok" syringe; a 10 mL syringe was used for trimethyl orthoacetate. In the case of ethylene orthocarbonate, the evaporator/sublimator was filled with the solid ethylene orthocarbonate. Workup of products following removal of hydrogen fluoride consisted of vacuum line fractionation, infrared assay of fractions, gas chromatographic separation of components using 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). Following gas chromatographic separation (Bendix Model 2300, subambient multicontroller) products were collected, transferred to the vacuum line, assayed, and characterized by vapor phase infrared spectrophotometry (PE 1330) and by ^{19}F nuclear magnetic resonance spectrometry (JEOL FX90Q, omniprobe) in CDCl_3 with 1% CFCl_3 internal standard. Electron impact (70 eV) high resolution electron impact mass spectrometry [VG Instruments ZAB-EQ; data format: m/z +/- deviation from exact mass in millimass units (% of base peak intensity) molecular composition of peak] was performed on each purified sample. The atoms permitted were ^{13}C , C, H, F and O; none of the compounds cations computed H containing species within 20 millimass units. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Reagents Tetramethyl orthocarbonate (99%, Aldrich) was used as received. Ethylene orthocarbonate was prepared via the reaction of tetramethyl orthocarbonate with ethylene glycol in the presence of p-toluenesulphonic acid [19]. Trimethyl orthoacetate (99%, Aldrich) was used as received.

TABLE 1

TYPICAL AEROSOL FLUORINATION REACTION PARAMETERS^a

Starting Compound	Fluorine Flow mL/m		Helium Diluent mL/m		Reaction Temp. °C		Main Helium Carrier mL/m
	Reactor Mod. 1	Mod. 2	Reactor Mod. 1	Mod. 2	Reactor Mod. 1	Mod. 2	
Tetramethylorthocarbonate	10	20	30	150	150	150	550
Ethylene orthocarbonate	20	20	--	150	150	150	800
Trimethyl orthoacetate	41	55	--	340	340	---	500

Starting Compound	Hydrocarbon Throughput millimoles/hr (H.C. carrier)	Overall ^b Stoichiometry hc:F ₂	Percent F ₂ Conc. Final Stage	Reaction Time ^c Sec.	Product Yield % Theoretical
Tetramethylorthocarbonate	3.9 ^d	1:38	3.7%	50	8%
Ethylene orthocarbonate	2.2 ^e	1:44	2.0%	40	17%
Trimethyl orthoacetate	11.8 ^f	1:22	4.8%	25	24%

^a See references 1, 2 and 11 for the significance of these parameters.

^b One milliliter/minute F₂ delivers 2.44 mmol/h F₂.

^c Reactor volume/total flows; reactor volume = 1355 cc; 761 cc (orthoacetate).

^d Total evaporator flow = 550 mL/m (500 mL/m primary, 50 mL/m secondary).

^e Total evaporator flow = 750 mL/m (700 mL/m primary, 50 mL/m secondary).

^f Total evaporator flow = 530 mL/m (50 mL/min primary, 30 mL/min secondary).

Tetramethyl orthocarbonate A pump speed corresponding to 3.9 mmol/h delivered 2.9 mL (3.0g, 21.8 mmol) of tetramethyl orthocarbonate over a 5.7 h period. From the crude product (2.08 g) was isolated 0.63 g (1.79 mmol, 8.2%, 7.67g theory) pure perfluorotetramethyl orthocarbonate based on total moles tetramethyl orthocarbonate injected (GLC temperature program: -35° , 7 min; 2°C/min to 0°C, 1 min; 15°C/min to 180°C). (CF₃O)₄C: IR (cm⁻¹) 1320vs, 1260vs, 1225s, 1215vs, 1100vs, 920m, 885w, 730m; High Resolution Mass Spectrometry major mass cations: 267.977 -3.8 mmu (3.63) ¹³CC₃F₉O₃; 266.975 -4.6 mmu, (50.51) C₄F₉O₃; 112.987 -2.4 mmu (24.64) C₂F₃O₂; 68.997 -2.0 mmu (100) CF₃. NMR ϕ = -56.67 ppm (s); Elemental Analysis: Calculated for C₅F₁₂O₄, C 17.06, F 64.76; Found C 13.86, F 65.55*.

Also isolated from the crude product was 1.24 g (4.34 mmol, 19.9%, 6.23 g theory) perfluorotrimethyl orthoformate. (CF₃O)₃CF: IR (cm⁻¹) 1320s, 1300vs, 1230vs, 1175m, 1105vs, 910m, 730m; High Resolution Mass Spectrometry major mass cations: 201.984 -2.2 mmu (0.71) ¹³CC₂F₇O₂; 200.984 -6.1 mmu (24.25) C₃F₇O₂; 68.998 -2.6 mmu (100) CF₃. ¹⁹F NMR resonances occur at ϕ CF₃ = -57.14 ppm (d), ϕ CF = -58.85 ppm (dectet), J = 9.76 Hz.

Ethylene orthocarbonate Ethylene orthocarbonate (2.06 g) was loaded into the sublimator. The sublimator was maintained at a temperature of 125°C throughout the 4 hours duration of the run. The reaction was stopped, and upon opening the reactor 0.89 g of unreacted ethylene orthocarbonate was recovered. The crude products were fractionated through -78°C and -123°C cold traps and 0.35 g pure perfluoroethylene orthocarbonate was isolated from the -78°C trap (GLC temperature program: -20°C, 5 m; 5°C/m to 0°C for 1 m; 5°C/m to 180°C). An additional 0.06 g perfluoroethylene orthocarbonate was recovered from the -123°C trap mixed 60:40 with a second component presumed to be

*Elemental analysis values have been repeated many times, values tend to be low for carbon and for F and vary with the same sample.

perfluoroethylene carbonate. Based on the 1.17 g (8.9 mmol) of ethylene orthocarbonate actually reacted, the 0.41 g (1.49 mmol) of perfluoroethylene orthocarbonate isolated represents a 16.8% yield (2.45g theory). $\text{[OCF}_2\text{CF}_2\text{O-C-OCF}_2\text{CF}_2\text{O]}$: IR (cm^{-1}) 1235s, 1170s, 1130vs, 1090m, 1030m, 820w, 760m; High Resolution Mass Spectrometry major mass cations: 256.972 -3.7 mmu (0.78) $\text{C}_5\text{F}_7\text{O}_4$; 209.975 -0.3 mmu (9.00) $\text{C}_4\text{F}_6\text{O}_3$; 144.986 +0.4 mmu (1.14) $^{13}\text{CC}_2\text{F}_4\text{O}_2$; 143.986 -3.5 mmu (30.55) $\text{C}_3\text{F}_4\text{O}_2$, 100.997 -0.3 mmu (6.62) $^{13}\text{CCF}_4$; 99.995 -1.0 mmu (100.00) C_2F_4 ; 68.996 -0.4 mmu (47.80) CF_3 ; 65.991 0.6 mmu (5.66) CF_2O ; 49.997 -0.5 mmu (52.75) CF_2 ; 46.995 -1.5 mmu (22.57) CFO. ^{19}F NMR resonance occurs at $\phi = -87.68$ ppm (s); Elemental Analysis: Calculated for $\text{C}_5\text{F}_8\text{O}_4$; C 21.76, F 55.06; Found C 20.53, F 55.03.

Trimethyl orthoacetate A pump speed of 1.5 mL/h delivered 6.0 mL (5.6-6g, 47.1 mmol) of trimethyl orthoacetate over a four hour period. The crude product (9.1g) was vacuum fractionated through -78°C , -131°C and -196°C traps. The contents of each trap were refractionated until all carbonyl fluoride had been removed. The fractions were collected and weighed. The residual -78°C trap contained 2.0g of pure (by glc) perfluoro-1,1-dimethoxyethane, two additional 0.5g fractions were added during refractionation of the -131°C fractions (3.0g, 11.1 mmol, 23.6% yield). The -196°C trap accumulated 6.0g (90.9 mmol) of carbonyl fluoride. The -131°C trap contained 0.5g of a mixture of perfluorinated esters and an ether which appears to be perfluorinated methyl ethyl ether. $\text{CF}_3\text{CF}(\text{OCF}_3)_2$: IR (cm^{-1}) 1385w, 1300vs, 1255vs, 1220sh, 1168s, 1130vs, 1105m, 933w, 898w, 760w. High Resolution Mass Spectrometry major mass cations: 200.979 +0.0 mmu (12.24) $\text{C}_3\text{F}_7\text{O}_2$; 184.986 -2.5 mmu (26.88) $\text{C}_3\text{F}_7\text{O}$; 97.995 -1.1 mmu (1.87) $^{13}\text{CCF}_3\text{O}$; 96.991 -1.0 mmu (68.61) $\text{C}_2\text{F}_3\text{O}$. ^{19}F NMR: -58.44 ppm (3) d (11.5 Hz); -89.77 ppm (2) s; -103.79 ppm (1) heptet (11.5 Hz).

RESULTS AND DISCUSSION

The major products collected from the aerosol direct fluorination of tetramethyl orthocarbonate were perfluorotrimethyl orthoformate and perfluorotetramethyl orthocarbonate, which constituted 59% and 30% of the total products, other than carbonyl fluoride, collected by weight, respectively. The low yield of perfluorotetramethyl orthocarbonate is a result of the ease of beta scission of the initial radical formed by hydrogen abstraction by fluorine, $(\text{CH}_3\text{O})_3\text{COCH}_2$, which rapidly loses $\text{O}=\text{CH}_2$ forming the $(\text{CH}_3\text{O})_3\text{C}\cdot$ radical which leads to the major isolated product. Apparently the presence of fluorine on the molecule formed by monofluorination retards somewhat a second beta scission. Despite the difficulty in obtaining reproducible elemental analyses, even on the same sample and the noninformative nature of the ^{19}F NMR spectra (all fluorines are equivalent), the characterization is unequivocal by high resolution mass spectrometry. The major cation at 287 m/z is unequivocally $\text{C}_4\text{F}_9\text{O}_3$ which corresponds to the perfluorinated trimethoxymethyl cation, $(\text{CF}_3\text{O})_3\text{C}^+$, which corresponds to the loss of a trifluoromethoxy group. Other oxygen containing cations support this characterization. The infrared spectrum looks superficially very much like perfluorodimethyl ether but the retention time on the QF-1 column is different.

The major product, perfluorotrimethyl orthoformate has one of the lowest methine fluorine chemical shifts on record. This shift at -58.86 ppm is a result of the downfield shift effect of the three methoxy groups bound to the methine carbon. The coupling ($J = 9.76$ Hz) of the three trifluoromethoxy groups to the methine fluorine results in a dectet of relative intensity one. The trifluoromethoxy groups resonance at -57.14 ppm, a doublet, has the expected relative intensity of nine. High resolution mass spectrometry unequivocally assigns the major mass cation at m/z 201 to $\text{C}_3\text{F}_7\text{O}_2$ which

corresponds to the expected perfluorodimethoxymethyl cation, $(CF_3O)_2CF^+$, which corresponds to loss of a trifluoromethoxy group, i.e. scission of the weakest bond to carbon.

The major product collected from the aerosol direct fluorination of ethylene orthocarbonate was perfluoroethylene orthocarbonate which was isolated in 17% yield. The beta scission of the initial radical produced by hydrogen abstraction is retarded by the cyclic structure. It is a well recognized fact that rings of small size can retard the formation of the linear transition state needed for a beta scission to occur [20]. The unequivocal assignments of the highest mass cation at m/z 257 as $C_5F_7O_4$, which corresponds to the molecular ion minus a fluorine, the major mass cation at 210 m/z which corresponds to the molecular ion minus $O=CF_2$, and the cation at 144 m/z corresponding to loss of OCF_2CF_2O from the molecular ion confirm the identity of the product. The base peak in the mass spectrum of perfluoroethylene orthocarbonate is C_2F_4 . The striking difference in the fragmentation pattern of perfluoroethylene orthocarbonate is due to the stabilization resulting from the cyclic structure.

The aerosol fluorination of trimethyl orthoacetate is interesting because it, unlike the orthocarbonates, undergoes complete beta scission of the parent structure. We had initially presumed that since orthocarbonates could be synthesized despite the fact that three alkoxy groups were present to stabilize the radical formed by beta scission, that orthoacetates which have only two alkoxy groups stabilizing the radical formed by beta scission would then be less likely to undergo beta scission. This presumption proved to be wrong as our results clearly suggest. The major product from the aerosol fluorination of trimethyl orthoacetate was perfluoro-1,1-dimethoxyethane formed in 24% yield. In this reaction done on the latest aerosol fluorinator configuration

the significance of the carbonyl fluoride formed was realized and so efforts were made to obtain a good mass balance [1]. The amounts of carbonyl fluoride produced (6.0g, 90.1 mmol) corresponds to an amount equivalent to the double beta scission of all remaining starting material. The product, perfluorinated methyl ethyl ether, was not isolated in sufficient quantity to confirm this conclusion. The 0.5 grams of isolated material, other than carbonyl fluoride and the major product, was a mixture of perfluorinated carbonyl compounds with perfluorinated methyl ethyl ether making up only about half the isolated quantity. The presence in all of the reactions of involatile residues indicates that the formaldehyde produced by beta scission may not all be converted to carbonyl fluoride. In the trimethyl orthoacetate reaction it was possible to account for only 75% of the input mass on the basis of volatiles. The same situation existed in the earlier reactions also, but the mass balance was even poorer due to reactor design, the presence of significant amounts of involatile residues and the poor recovery of carbonyl fluoride.

In conclusion the aerosol fluorinator provides an acceptable route to perfluorinated orthocarbonates. The synthesis of other perfluorinated orthoesters apparently will be limited to systems in which the beta scission of radicals is less of a problem.

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