***cis,trans*-2,3-Diphenyl-1-(*p*-chlorobenzoyl)cyclopropane (8)**: mp 108–109 °C (hexane–benzene); IR ($CHCl_3$) 1670 cm^{-1}; mass spectrum (70 eV), *m/e* 332 (M^+); ^1H NMR ($CDCl_3$) δ 3.21 (dd, H_A, J_{AB} = 9.56 Hz), 3.32 (dd, H_B, J_{BC} = 5.27 Hz), 3.58 (dd, H_C, J_{AC} = 6.92 Hz), 7.3 (m, 12 H), 7.9 (m, 2 H). Anal. Calcd for $C_{22}H_{17}ClO$: C, 79.39; H, 5.14; Cl, 10.65. Found: C, 78.98; H, 5.23; Cl, 10.82.

***cis,trans*-2,3-Diphenyl-1-(*p*-bromobenzoyl)cyclopropane (9)**: mp 113–115 °C (hexane–benzene); IR ($CHCl_3$) 1670 cm^{-1}; mass spectrum (70 eV), *m/e* 376 (M^+); ^1H NMR ($CDCl_3$) δ 3.23 (d, 2 H), 3.56 (t, 1 H), 7.1–7.3 (m, 12 H), 7.63 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.1, 36.5, 38.0, 127.0, 127.1, 128.3, 128.8, 129.1, 129.7, 131.9, 194.0. Anal. Calcd for $C_{22}H_{17}BrO$: C, 70.04; H, 4.45. Found: C, 70.12; H, 4.27.

***cis,trans*-2,3-Diphenyl-*trans*-2-ethyl-1-benzoylcyclopropane (10)**: mp 135–137 °C (ethanol); IR ($CHCl_3$) 1670 cm^{-1}; mass spectrum (70 eV), *m/e* 326 (M^+); ^1H NMR ($CDCl_3$) δ 0.68 (t, 3 H), 1.65 (m, 2 H), 3.3 (d, H_B, J_{BC} = 5.93 Hz), 3.75 (d, H_C), 7.3 (m, 13 H), 8.0 (m, 2 H). Anal. Calcd for $C_{24}H_{22}O$: C, 88.17; H, 6.78. Found: C, 88.31; H, 6.90.

***cis,trans*-2,3-Diphenyl-1-(*p*-methoxybenzoyl)cyclopropane (11)**: mp 104–105 °C (ethanol); IR ($CHCl_3$) 1670 cm^{-1}; mass spectrum (70 eV), *m/e* 328 (M^+); ^1H NMR ($CDCl_3$) δ 3.85 (s, 3 H), 3.24 (dd, H_A, J_{AB} = 9.23 Hz), 3.32 (dd, H_B, J_{BC} = 5.94 Hz), 3.56 (dd, H_C, J_{AC} = 6.92 Hz), 7.2 (m, 12 H), 7.95 (m, 2 H). Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.99; H, 6.23.

***cis,trans*-2,3-Diphenyl-1-(*p*-fluorobenzoyl)cyclopropane (12)**: mp 101–102 °C (hexane); IR ($CHCl_3$) 1680 cm^{-1}; mass spectrum (70 eV), *m/e* 316 (M^+); ^1H NMR ($CDCl_3$) δ 3.2 (dd, H_A, J_{AB} = 9.56 Hz), 3.27 (dd, H_B, J_{BC} = 5.6 Hz), 3.54 (dd, H_C, J_{AC} = 6.59 Hz), 7.3 (m, 12 H), 7.9 (m, 2 H). Anal. Calcd for $C_{22}H_{17}FO$: C, 83.52; H, 5.41, F, 6.00. Found: C, 83.66; H, 5.60; F, 6.22.

***cis,trans*-2,3-Diphenyl-1-pivaloylcyclopropane (13)** was obtained by reaction of benzalpinacolone with 1 equiv of benzaldehyde phosphazine[5] for 16 h: 32% yield; mp 90–92 °C (pentane–benzene; IR ($CHCl_3$) 1690 cm^{-1}; mass spectrum (70 eV), *m/e* 278 (M^+); ^1H NMR ($CDCl_3$) δ 1.0 (s, 9 H), 2.92 (dd, H_B, J_{AB} = 9.23 Hz), 3.0 (dd, H_A, J_{AC} = 6.92 Hz), 3.36 (dd, H_C, J_{BC} = 5.27 Hz), 7.26 (m, 10 H). Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.96. Found: C, 86.26; H, 8.07.

***cis*-2-Phenyl-*trans*-3-*tert*-butyl-1-benzoylcyclopropane (14)** was obtained by reaction of β-*tert*-butylchalcone with 2 equiv of benzaldehyde phosphazine[5] for 18 h: 27% yield; mp 112–114 °C (petroleum ether–benzene); IR ($CHCl_3$) 1665 cm^{-1}; mass spectrum (70 eV), *m/e* 278 (M^+); ^1H NMR ($CDCl_3$) δ 1.05 (s, 9 H) 2.45 (dd, H_C, J_{AC} = 7.45 Hz), 2.84 (dd, H_A, J_{AB} = 9.55 Hz), 2.97 (dd, H_B, J_{BC} = 5.93 Hz), 7.4 (m, 8 H), 7.9 (m, 2 H). Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.95. Found: C, 86.06; H, 7.87.

Cyclopropane (3) via Pyrazoline (15). Benzaldehyde hydrazone (6.5 g, 0.054 mol) in ether (20 mL) was added dropwise to a stirred cooled suspension of yellow mercuric oxide (23.3 g, 0.108 mol) in ether (100 mL). After the addition was complete (15 min), aqueous saturated sodium hydroxide solution (5.0 mL) was added. The suspension, which slowly turned wine red, was stirred (20 min) and gravity filtered through a fluted filter full of sodium sulfate (anhydrous). To the clear, wine-red solution of phenyldiazomethane was added chalcone (10 g, 0.048 mol) in ether (100 mL). The mixture was stirred for 4.5 h during which a slight amount of nitrogen evolution was observed and the mixture had decolorized. The solution was then concentrated to a light yellow oil and triturated with 95% ethanol (20 mL). The resulting white crystalline precipitate was collected by filtration, affording 4.2 g (26%) of **15**: mp 130–132 °C dec; IR ($CHCl_3$) 1660, 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.5 (d, 1 H, J_{AB} = 5.9 Hz), 4.8 (d, 1 H), 6.8 (s, 1 H), 7.5 (m, 13 H), 8.2 (m, 2 H).

A suspension of **15** (0.250 g, 0.76 mmol) in dry *n*-butyl ether (10 mL) was heated to reflux (12 h) by using an oil bath. The *n*-butyl ether was removed from the yellow reaction mixture by a rotary evaporator and then a vacuum pump (room temperature). The residual oil was chromatographed on silica gel (hexane–ether, 8:2). The fractions which contained the cyclopropane were combined, concentrated, and then triturated with 95% ethanol, affording **3** as white crystalline needles: mp 153–154 °C; 0.14 g (62%). This product was identical with that obtained from the phosphoranylidenehydrazone reaction.

3-Benzoyl-4-phenyl-5,5-diethyl-Δ²-pyrazoline (16). 3-Pentanone triphenylphosphoranylidenehydrazone[5] (2.0 g, 5.5 mmol) was added to a suspension of chalcone (1.15 g, 5.5 mmol) in dry *n*-butyl ether (50 mL). The mixture was heated to reflux for 8.0 h, the reaction solvent removed via a rotary evaporator and then a vacuum pump, and treated with iodomethane (3 mL, 48 mmol) in ether (50 mL), affording a crystalline precipitate of methyltriphenylphosphonium iodide. The precipitate was removed by filtration through a 20 × 100 mm column of silica, and the filtrate was concentrated to an oil and triturated with 95% ethanol (20 mL). The resulting crystals were collected and recrystallized from hexane/benzene to yield 0.404 g (24%) of 3-benzoyl-4-phenyl-5,5-diethyl-Δ²-pyrazoline: mp 118–120 °C; ^1H NMR ($CDCl_3$) δ 0.5–1.9 (m, 10 H, *gem*-diethyl), 4.3 (s, 1 H, benzyl), 6.45 (br s, 1 H, NH), 7.0–7.5 (m, 8 H, phenyl), 8.1 (m, 2 H, *o*-benzoyl); IR ($CHCl_3$) 1655 cm^{-1}. Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.39; H, 7.23; N, 9.14. Found: C, 78.17; H, 7.27; N, 8.98.

Acylpyrazolines **17** and **18** could be prepared analogously. **17**: oil; 11% yield; ^1H NMR ($CDCl_3$) δ 0.5–1.8 (m, 10 H), 2.35 (s, 3 H), 4.0 (s, 1 H), 6.3 (s, 1 H), 7.3–7.8 (m, 5 H); IR ($CHCl_3$) 1655 cm^{-1}. **18**: oil; 5% yield; ^1H NMR ($CDCl_3$) δ 0.75 (s, 3 H), 0.90 (s, 9 H), 4.55 (s, 1 H), 6.7 (s, 1 H), 7.0–7.5 (m, 8 H), 7.58–8.15 (m, 2 H); IR ($CHCl_3$) 1650 cm^{-1}.

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Registry No. **1** (R^1, R^2 = H), 1103-87-3; **1** (R^1 = 4-CH_3; R^2 = H), 86118-52-7; **1** (R^1 = H; R^2 = CH_3), 2734-98-7; **1** (R^1 = H; R^2 = C_2H_5), 53813-64-2; **3**, 26597-09-1; **4**, 86118-53-8; **5**, 86161-60-6; **6**, 86161-61-7; **7**, 86118-54-9; **8**, 86118-55-0; **9**, 86118-56-1; **10**, 86118-57-2; **11**, 86118-58-3; **12**, 86118-59-4; **13**, 86118-60-7; **14**, 86118-61-8; **15**, 56445-39-7; **16**, 86118-62-9; **17**, 86118-63-0; **18**, 86118-64-1; (*E*)-PhCOCH=CHPh, 614-47-1; (*E*)-4-$CH_3C_6H_4COCH$=CHPh, 14802-30-3; (*E*)-PhCOCH=$CHC_6H_4CH_3$-4, 22252-14-8; (*E*)-4-ClC_6H_4COCH=CHPh, 22966-22-9; (*E*)-4-BrC_6H_4COCH=CHPh, 22966-23-0; (*E*)-4-$CH_3OC_6H_4COCH$=CHPh, 22966-19-4; (*E*)-4-FC_6H_4COCH=CHPh, 22966-25-2; (*E*)-*t*-BuCOCH=CHPh, 538-44-3; (*E*)-PhCOCH=CHBu-*t*, 29569-93-5; $PhCH{=}NNH_2$, 5281-18-5; PhCDO, 3592-47-0; 4-$CH_3C_6H_4CDO$, 13277-99-1; $PhCOCH_3$, 98-86-2; (*E*)-PhCOCH=CDPh, 32461-19-1; (*E*)-PhCOCH=$CDC_6H_4CH_3$-4, 86118-66-3; (*E*)-PhCOCD=CDPh, 23057-96-7; (*E*)-PhCOCD=$CDC_6H_4CH_3$-4, 86118-69-6; 3-pentanone triphenylphosphoranylidenehydrazone, 86118-65-2; 2-phenyl-1,3-dithiane, 5425-44-5; 2-*p*-tolyl-1,3-dithiane, 56637-44-6; *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane-*3-d*, 86118-67-4; *trans*-2-*p*-tolyl-*cis*-3-phenyl-1-benzoylcyclopropane-*2-d*, 86118-68-5; *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane-*1,3-d_2*, 86118-70-9; *trans*-2-*p*-tolyl-*cis*-3-phenyl-1-benzoylcyclopropane-*1,2-d_2*, 86118-71-0.

Supplementary Material Available: Scheme showing stereochemistry with deuterium-labeled chalcones (2 pages). Ordering information is given on any current masthead page.

Aerosol Direct Fluorination: Syntheses of Perfluoro Ketones

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

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Table I. Typical Aerosol Fluorination Reaction Parameters

starting compd	F flow, mL/m				He diluent, mL/m			
	reactor		mod 1	mod 2	reactor		mod 1	mod 2
3-pentanone	20	20			20	20		
4-heptanone	20	30			20	20		
3-heptanone[c]		20	20	30		150	150	150
cyclopentanone	10	15	20		30	30	30	

[a] One milliliter/minute F_2 delivers 2.44 mmol/h F_2. [b] *F*-Pentanoyl fluoride. [c] A flash evaporator hydrocarbon injector

to alkanes, ethers, cycloalkanes, and ketals has been demonstrated.[1] The extension of this novel process to ketones provides direct access to analogue perfluoroketones in modest yields, a feat not realized by other direct fluorination methods to any significant degree,[2] although indirect procedures have proven effective for selected cases.[3-8]

Bigelow and Holub, in a comparison of direct (catalytic) fluorination and the cobalt(III) fluoride (Fowler) process, reported that acetone, methyl ethyl ketone, and cyclopentanone could be fluorinated with elemental fluorine to their perfluoro analogues, albeit in poor yields; the cobalt (III) fluoride process, however, cleaved the ketones at a very early stage in the reaction.[2]

Because of the difficulty of producing perfluoro ketones directly, numerous indirect methods have been developed.[3-8] For example, the deficiency of the cobalt(III) fluoride process in the production of perfluoro ethers can be ameliorated if the ether is already fluorinated on one side.[4] The subsequent sulfuric acid hydrolysis of these halomethyl perfluorocycloalkane ethers (prepared from methanol addition to perfluorocycloalkenes followed by cobalt(III) fluoride fluorination) yielded perfluorocyclopentanone and perfluorocyclohexanone.[4] A similar process, which uses chlorination followed by KF–tetramethylene sulfone metathesis instead of cobalt(III) fluoride fluorination prior to hydrolysis has been reported by Anello et al.[5] Another method for the production of perfluoro ketones is the decomposition over alumina of the corresponding perfluoroalkylene epoxides prepared from the corresponding cyclic and acyclic alkenes.[6] Perhaps the most useful processes on a research scale are the condensation of methyl and ethyl perfluoro carboxylates with sodium,[7] the related reaction of perfluoro carboxylic acids with sodium alkoxide,[8] and the reactions of ethyl perfluoroalkanecarboxylates with perfluoroalkyl Grignard or lithium reagents[9] to produce the symmetrical bis(perfluoroalkyl) ketones and in the latter case potentially the unsymmetrical ketones.

Results and Discussion

The efficacy of the aerosol process for the direct fluorination of ketones is somewhat surprising. LTG (low-temperature-gradient) fluorinations have not successfully fluorinated ketones under the usual conditions.[10] The aerosol process is very rich in fluoride ion; thus fluoride-catalyzed oxidation of the ketone carbonyl group might be expected to produce fluoroxy compounds.[11] It might also be expected that the photochemical finishing stage of the aerosol process would result in photolytic cleavage of the ketone.[12] In reality none of the above problems were manifested in the results. In fact the high concentration of fluoride ion may be beneficial in that the acidity of the medium due to endogeneous hydrogen fluoride is reduced, thus minimizing acid-catalyzed condensation reactions.[13]

In each of the reactions the perfluoro ketone was the major product collected. Of the products collected *F*-3-pentanone, *F*-3-heptanone, and *F*-4-heptanone were 71%, 59%, and 92% of the total by weight; although these numbers are impressive, they obscure a troublesome problem with all of the ketone reactions to date. The aerosol system is dependent on the generation of a particulate aerosol that is ideally crystalline and monodisperse (uniform size) and with little tendency to aggregate. In reality only a few compounds produce near perfect aerosols exhibiting all of the previous properties. Most compounds that produce excellent aerosols are highly symmetrical and pack well in a crystal lattice. Examples are neopentane, adamantane, cycloalkanes, cyclic ethers, and most highly branched, geometrically uniform molecules. Normal alkanes and especially their functional derivatives deviate in varying degrees from this ideal. 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 the molecules deviate from this ideal shape, the percent yields based on throughput begin to fall because of 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 or adjustments are made due to recovered unreacted or partially reacted materials, the yield of *F*-3-pentanone, *F*-3-heptanone, and *F*-4-heptanone are 13%, 13%, and 23%, respectively. It should, however, be emphasized at this point that in virtually all reactions, fragmentation amounts to less than 15% of the total

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Table I (*Continued*)

rctn temp, °C			main He carrier, mL/m	hydrocarbon throughput, mmol/h (HC carrier)	overall[a] stoichiometry, HC:F_2	% F_2 concn, final stage	reactor vol, mL (α length)	rctn time, s	product distrib, % collected	product yield, % theoret
reactor	mod 1	mod 2								
−20	−10	10	600	2.0 (70)	1:49	5.3	1355	108	71%	13
−30	−20	10	750	2.0 (165)	1:61	5.0	1355	81	92%	23
−40	−30	0	500	3.5 (500)	1:56	4.6	*d*	*d*	59%	13
−40	−30	10	750	2.1 (112)	1:55	4.5	1355	82	61%	24[b]

fed by syringe pump was used in this reaction. [d] New reactor volume not calibrated, similar to previous reactor.

throughput, although in the 3-heptanone fluorination, *F*-*n*-butane was isolated in yields approaching that of *F*-3-heptanone.

Although fragmentation is minimal, occasionally almost total cleavage will occur in a reaction. An example of this is the attempted fluorination of cyclopentanone. The major product collected (61% of the total) was *F*-pentanoyl fluoride in a yield based on total throughput of 24%. The only other product of significance was *F*-*n*-butane (11% of collected product) and numerous very small peaks collectively identified as partly fluorinated acid fluorides from their infrared spectra.

The quantities of materials run were small to achieve more nearly ideal conditions. Throughputs of up to 10 mmol/h can be achieved with most compounds on the present reactors of 0.5-in. cross section; these throughputs usually produce somewhat lower yields and product purity although larger amounts, up to 10 g of fluorocarbons, have been produced this way.

Although considerably more work is necessary, primarily in optimization of aerosol generation before aerosol direct fluorination can be considered a general route to perfluoro ketones, clearly the progress so far indicates that this novel direct fluorination process has overcome many obstacles to a direct synthesis of perfluoro ketones.

Experimental Section

The basic aerosol fluorinator design and a basic description of the process is presented elsewhere.[1] 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 m × $^3/_8$ in. 13% fluorosilicone QF-1 (Analabs) stationary phase on 60–80-mesh, acid-washed, Chromosorb P conditioned at 225 °C (12 h) or a 4 m × $^3/_8$ in. 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, PE1330, electron-impact (70 eV) and chemical-ionization (CH_4 plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980 A MS, 5934A computer), and ^1H and ^{19}F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in $CDCl_3$ with 1% $CFCl_3$ internal standard. The above characterizations are available as *supplementary material*.

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 cm^3/min helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 2 mmol/h. Details of the aerosol fluorination parameters are given in Table I. For a 4-h, photochemically finished run, 0.38 g of crude product was separated gas chromatographically on the fluorosilicone QF-1 column (−5 °C/2 m, 1 °C/m to 10 °C/1 m, 30 °C/m to 180 °C/5 m), producing 0.27 g of *F*-3-pentanone (71%, Table I), 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 cm^3/m of helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 2 mmol/h. Details of the aerosol fluorination parameters are given in Table I. For a 4-h, photochemically finished run, 0.734 g of crude product was separated on the fluorosilicone QF-1 column (30 °C/1 m, 2 °C/m to 60 °C/1 m, 50 °C/m to 180 °C/5 m), producing 0.675 g of *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 cm^3/m helium through 50 mL of the material contained in a sparge tube evaporator produces a throughput of 2.1 mmol/h. Details of the aerosol fluorination parameters are given in Table I. For a 3-h, photochemically finished reaction, 0.62 g of crude product was separated on the fluorosilicone QF-1 column (10 °C/1 m, 1 °C/m to 30 °C/1 m; 20 °C/m to 100 °C/10 m), producing 0.378 g of *F*-pentanoyl fluoride (61%) with a yield based on theoretical throughput of 24%. Cyclopentanone was again found in the reactor on warming.

Aerosol Fluorination of 3-Heptanone. 3-Heptanone (Aldrich) was used as received. Its vapor pressure was too low to get an acceptable throughput by evaporation at room temperature and a modified aerosol generator was adapted to a flash evaporator fed by a syringe pump (SAGE Model 341a) driving a 5.000-mL Precision Sampling Corp, "Pressure Lok" syringe. A pump speed corresponding to 3.5 mmol/h was established and 2.95 mL (2.41 g, 21.2 mmol) of 3-heptanone was delivered over a 6-h period. Details of the aerosol fluorination parameters are given in Table I. From the crude product (1.65 g) was isolated 0.98 g (59%) of pure *F*-3-heptanone (GLC temperature program on the QF-1 column (25 °C/2 min, 1.5 °C/min to 60 °C/1 min, 50 °C/min to 180 °C/20 min), corresponding to a yield of 13% based on total 3-heptanone injected. Much of the 3-heptanone was recovered unchanged.

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Registry No. 3-Pentanone, 96-22-0; 4-heptanone, 123-19-3; cyclopentanone, 120-92-3; 3-heptanone, 106-35-4; *F*-3-pentanone, 684-32-2; *F*-4-heptanone, 378-90-5; *F*-pentanoyl fluoride, 375-62-2; *F*-3-heptanone, 85894-30-0; *F*-*n*-butane, 355-25-9.

Supplementary Material Available: Characterization data for products (IR, MS, ^{19}F NMR; 3 pages). Ordering information is given on any current masthead page.