with the 2-chloroethoxy derivative where ion b was small. In fact, the mechanism to ion b shown in Scheme I would, in the 2-chloroethoxy case, necessitate the improbable loss of a methylene group. Therefore, ion b in the latter case must arise by a different mechanism, perhaps by exchange of the *tert*-butyl and chlorine groups followed by the loss of a neopentyl radical.[9] On the other hand, since ion c is the base peak in this same compound it must be formed by a mechanism different than that shown in Scheme I. It seems probable, at least in the 2-chloroethoxy derivative (and possibly in the other examples), that ion c arises from ion a', by a mechanism similar to that shown by Diekman, et al.[10] for 1,2-bis(trimethylsiloxy)ethane (see Scheme II). Indeed, this was substantiated by the observation of a metastable peak at m/z 63.1 for the transformation a' → c. It appears that the importance of ion c diminishes with an increase in the distance between chlorine and silicon (see Table I).

Not surprisingly, when the mass spectra of the *tert*-butyldimethylsilyl ethers of both 3-bromopropanol and 4-bromobutanol were examined, an analogous bromine to silicon migration was observed. From this work and that of others,[3] we suggest that organic chemists examining the mass spectra of halogenated *tert*-butyldimethylsilyl ethers might observe ions such as b and c, in which halogen has migrated to silicon.

Experimental Section

^{1}H NMR (89.55 MHz) and ^{13}C NMR (22.5 MHz) spectra were recorded on a JEOL FX-90Q spectrometer using $CDCl_3$ as solvent and Me_4Si as an internal standard. Low-resolution mass spectra were obtained on a Finnigan 3200 GC spectrometer (column conditions, OV-17, injector at 200 °C, oven at 90 °C, programmed at 10°/min), the metastable data were obtained on an LKB Model 9000 spectrometer at both 15 and 70 eV, and high-resolution data were obtained from the Massachussetts Institute of Technology Mass Spectrometry Facility on a Varian MAT 731 spectrometer in the electron-impact mode. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The petroleum ether used had bp 38–56 °C.

(3-Chloropropoxy)dimethyl-*tert*-butylsilane (1) (General Procedure). A solution of 3-chloropropanol (5 mL) in dichloromethane (5 mL) was washed with deionized water (1 mL), 5% $NaHCO_3$ solution (1 mL, until the washes were basic), and a saturated NaCl solution (1 mL). The organic layer was dried ($MgSO_4$), concentrated and purified by Kugelrohr distillation (7 mm).[11]

tert-Butyldimethylsilyl chloride (1.99 g, 13.2 mmol) and imidazole (0.90 g, 13.2 mmol) were dissolved in anhydrous DMF (5 mL) under N_2. After 5 min, freshly distilled 3-chloropropanol (1.04 g, 11.0 mmol) was added. The reaction was allowed to stir overnight at room temperature under N_2. Workup involved addition of diethyl ether (30 mL) and washing the organic layer with deionized water (3 × 2.5 mL). The combined aqueous washes were reextracted with an equal volume of diethyl ether. The combined ethereal layers were dried ($MgSO_4$), and concentrated in vacuo, and the resulting oil was purified by column chromatography[7] on silica gel 60 (Merck 0.06–0.20 mm, column dimensions 1.5 × 45 cm) using 100 mL of petroleum ether initially, and the product was then eluted with petroleum ether/diethyl ether (70:30). The purest fraction afforded the following data: ^{1}H NMR δ 3.75 (t, J = 6 Hz, CH_2O),[12] 3.65 (t, J = 6 Hz, CH_2Cl),[12] 1.95 (apparent pentant, J = 6 Hz, $CH_2CH_2CH_2$), 0.90 (s, $C(CH_3)_3$), 0.07 (s, $Si(CH_3)_2$); ^{13}C NMR δ 59.4 (CH_2O), 41.6 (CH_2Cl), 35.6 ($CH_2CH_2CH_2$), 25.9 ($C(CH_3)_3$), 18.3 ($C(CH_3)_3$), −5.4 ($Si(CH_3)_2$).[13] Anal. Calcd for $C_9H_{21}ClOSi$: C, 51.79; H, 10.07. Found: C, 51.87; H, 10.02.

(2-Chloroethoxy)dimethyl-*tert*-butylsilane. Following the general procedure above afforded the corresponding 2-chloroethoxy derivative, which gave the following physical data: ^{1}H NMR δ 3.44 (t, J = 5 Hz, CH_2O),[12] 3.17 (t, J = 5 Hz, CH_2Cl),[12] 0.80 (s, $C(CH_3)_3$), 0.08 (s, $Si(CH_3)_2$); ^{13}C NMR δ 63.8 (CH_2O), 45.1 (CH_2Cl), 25.9 ($C(CH_3)_3$), 18.4 ($C(CH_3)_3$), −5.3 ($Si(CH_3)_2$).[13] Anal. Calcd for $C_8H_{19}ClOSi$: C, 49.35; H, 9.77. Found: C, 49.32; H, 9.91.

[(4-Chlorobutyl)oxy]dimethyl-*tert*-butylsilane. Following the general procedure above afforded the corresponding (4-chlorobutyl)oxy derivative, which gave the following physical data: ^{1}H NMR δ 3.58 (apparent quartet, J = 6 Hz, 4 H, CH_2O, CH_2Cl), 1.75 (m, 4 H, CH_2CH_2), 0.88 (s, $C(CH_3)_3$), 0.04 (s, $Si(CH_3)_2$); ^{13}C NMR δ 62.4 (CH_2O), 45.1 (CH_2Cl), 30.3 (CH_2CH_2Cl), 29.6 (CH_2CH_2O), 26.6 ($C(CH_3)_3$), 18.4 ($C(CH_3)_3$), −5.2 ($Si(CH_3)_2$).[13] Anal. Calcd for $C_{10}H_{23}ClOSi$: C, 53.93; H, 10.34. Found: C, 54.17; H, 10.53.

[(5-Chloropentyl)oxy]dimethyl-*tert*-butylsilane. Following the general procedure above afforded the corresponding (5-chloropentyl)oxy derivative, which gave the following physical data: ^{1}H NMR δ 3.57 (apparent quartet, J = 6 Hz, 4 H, CH_2O, CH_2Cl), 1.78 (apparent pentant, J = 6 Hz, 4 H, $CH_2CH_2CH_2CH_2CH_2$), 1.53 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2$), 0.88 (s, $C(CH_3)_3$), 0.05 (s, $Si(CH_3)_2$); ^{13}C NMR δ 62.8 (CH_2O), 44.9 (CH_2Cl), 32.5, 32.1 ($CH_2CH_2CH_2CH_2CH_2$), 26.0 ($C(CH_3)_3$), 23.3 ($CH_2CH_2CH_2CH_2CH_2$, 18.3 ($C(CH_3)_3$), −5.3 ($Si(CH_3)_2$).[13] Anal. Calcd for $C_{11}H_{25}ClOSi$: C, 55.81; H, 10.57. Found: C, 55.59; H, 10.68.

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Registry No. $(CH_3)_3CSi(CH_3)_2O(CH_2)_2Cl$, 89031-81-2; $(CH_3)_3CSi(CH_3)_2O(CH_2)_3Cl$, 89031-82-3; $(CH_3)_3CSi(CH_3)_2O(CH_2)_4Cl$, 89031-83-4; $(CH_3)_3CSi(CH_3)_2O(CH_2)_5Cl$, 85514-44-9; 3-bromopropyl *tert*-butyldimethylsilyl ether, 89031-84-5; 4-bromobutyl *tert*-butyldimethylsilyl ether, 89043-32-3; *tert*-butyldimethylsilyl chloride, 18162-48-6; 2-chloroethanol, 107-07-3; 3-chloropropanol, 627-30-5; 4-chlorobutanol, 928-51-8; 5-chloropentanol, 5259-98-3.

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

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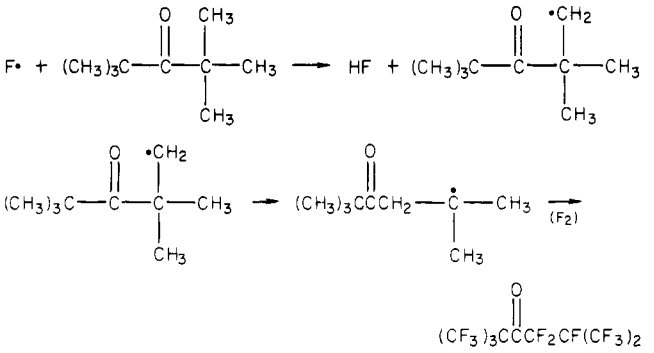
The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation. The application of this process

to alkanes, ethers, cycloalkanes, and ketals has been demonstrated.[1] Extension of this noval process to ketones has provided direct access to analogue perfluoro ketones in modest yields and has led to the successful perfluorination of methyl ketones[2] 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 analogues, which can be converted in good yields to the corresponding perfluoro cyclic ketones 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 occuring during the aerosol fluorination of ketones.

In general, routes to perfluoro ketones, 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 chloro carbons prior to fluorination, and the higher perchloro carbons are often difficult to prepare. Typical preparations of perfluoro ketones include the decomposition over Lewis acid catalysts of perfluoroalkyene epoxides[6-13] and the reaction of perfluoroalkyl carboxylates or perfluoroacyl chlorides with organometallic reagents such as perfluoropropyllithium, perfluoropropylmagnesium iodide, or perfluoropropylzinc iodide.[14-18] In contrast to the above, the aerosol direct fluorination method has provided direct access to perfluoro ketones from the relatively inexpensive hydrocarbon analogues.[3]

Whereas a number of straight-chain perfluoro ketones are known, relatively few branched perfluoro ketones 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 perfluoro ketones. Only two other branched perfluoro ketones have been reported in the literature: *F*-4-methyl-2-pentanone, formed via the Lewis acid catalyzed opening of *F*-3-methyl-2-butenyl epoxide,[10] and *F*-4-methyl-2-heptanone, formed via the treatment of *F*-2-(chlorosulfato)-4-methylheptane with potassium fluoride.[24]

Scheme I



Results and Discussion

The aerosol direct fluorination of 3,3-dimethyl-2-butanone produced *F*-3,3-dimethyl-2-butanone, 3-(difluoromethyl)-*F*-3-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 temperature 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 were 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 dihydryl 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 dihydryl 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 occuring 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

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initially formed primary radical to the more stable tertiary radical, followed by fluorination in the usual fashion (Scheme I). 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 noval 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 Experimental Section) consists of four multiplets of relative intensity 9:6:2:1 at ϕ −61.61, −71.82, −109.32, and −184.26 ppm (1% $CFCl_3/CDCl_3$ 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 ϕ −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 Section

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, and 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 phenylmethyl 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 (CH_4 plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980A MS, 5934A computer), and ^1H and ^{19}F nuclear magnetic resonance (JEOL FX90Q, Omniprobe) spectrometry in $CDCl_3$ with 1% $CFCl_3$ internal standard. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

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 I. From the crude product was isolated 0.238 g (23%) of *F*-3,3-dimethyl-2-butanone, 0.258 g (25%) of 3-(difluoromethyl)-*F*-3-methyl-2-butanone, and 0.134 g (13%) of 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 the amount of 3,3-dimethyl-2-butanone injected was 12%. The characterization of these new compounds is given below.

***F*-3,3-Dimethyl-2-butanone**, $CF_3^AC(O)C(CF_3^B)_3$: 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* (relative intensity) formula]: [CI] 317 (59) $C_6F_{12}OH$, M + H; 297 (84) $C_6F_{11}O$, M − F; 97 (100) C_2F_3O; 69 (58) CF_3; [EI] 181 (16) C_4F_7; 97 (21) C_2F_3O; 69 (100) CF_3. ^{19}F NMR [1% $CFCl_3/CDCl_3$] ϕ_A −73.88 ppm (d), ϕ_B = −61.12 (q), J_{AB} = 6.1 Hz. Anal. Calcd for $C_6F_{12}O$: C, 22.80; F, 72.13. Found: C, 21.37; F, 72.43.

3-(Difluoromethyl)-*F*-3-methyl-2-butanone, $CF_3^AC(O)C(CF_2^BH^C)(CF_3^D)_2$: 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* (relative intensity) formula]: [CI] 300 (8) $C_6F_{11}OH_3$, M + 2H; 164 (100) $C_4F_6H_2$; 97 (15) C_2F_3O; [EI] 231 (28) C_5F_9; 164 (33) $C_4F_6H_2$; 160 (61) C_4F_5OH; 97 (50) C_2F_3O; 69 (100) CF_3; 51 (38) CF_2H. ^{19}F NMR [1% $CFCl_3/CDCl_3$] ϕ_A −73.85 ppm (m), ϕ_B −126.69 (m), ϕ_D −62.05 (m). ^1H NMR δ_C +6.63 (t); J_{CF_2H} = 51.5 Hz.

3,3-Bis(difluoromethyl)-*F*-2-butanone, $CF_3^AC(O)C(CF_3^B)(CF_2^CH^D)_2$: 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* (relative intensity) formula]: [CI] 282 (100) $C_6F_{10}OH_4$, M + 2H; 212 (36) $C_5F_7OH_3$; 97 (65) C_2F_3O; 69 (43) CF_3; [EI] 212 (64) $C_5F_7OH_3$; 146 (41) C_6F_3OH; 142 (100) $C_4F_4OH_2$; 97 (35) C_2F_3O; 69 (85) CF_3; 51 (43) CF_2H. ^{19}F NMR [1% $CFCl_3/CDCl_3$] ϕ_A −74.61 ppm (m), ϕ_B −62.99 (m), ϕ_C −125.18 (m). ^1H NMR δ_D +6.59 ppm (t); J_{CF_2H} = 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 of 2,2,4,4-tetramethyl-3-pentanone delivered over a 2 h-period. Details of the aerosol fluorination parameters are given in Table I. From the crude product (0.346 g) was isolated 0.246 g (71%) of *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 (ultraviolet 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**, $(CF_3^A)_3CC(O)CF_2^BCF^C(CF_3^D)_2$: 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 [m/e (relative intensity) formula]: [CI] 483 (2) $C_{10}F_{18}OH_5$, M + CH_5; 467 (12) $C_9F_{18}OH$, M + H; 447 (54) $C_9F_{17}O$, M − F; 247 (55) C_5F_9O; 219 (100) C_4F_9; 201 (84) C_4F_8; 181 (98)

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Table I. Typical Aerosol Fluorination Reaction Parameters[a]

starting compound	fluorine flow, mL/min		helium diluent, mL/min		reaction temp, °C		main helium carrier, mL/min	hydrocarbon throughput mmol/h	overall[b] stoichiometry hc:F_2	percent F_2 concn, final stage	reaction time,[c] s	product distribution % collected	product yield % theoretical
	reactor	mod 1	reactor	mod 1	reactor	mod 1							
		mod 2		mod 2		mod 2							
3,3-dimethyl-2-butanone	10	20	150	150	−40	−30	600	2.8[e]	1:52	3.6	49	23	12
		30		150		10							
2,2,4,4-tetramethyl-3-pentanone	20	20	150	150	−30	−20	600	2.9[e]	1:67	4.8	49	71	9[d]
		40		150		10							

[a] See ref 1 and 25 for the significance of these parameters. [b] One milliliter/minute of F_2 delivers 2.44 mmol/h of F_2. [c] Reactor volume/total flows; reactor volume = 1355 mL. [d] Product is *F*-2,2,5-trimethyl-3-hexanone. [e] Total carrier flow through evaporator 550 mL/min (500 mL/min primary, 50 mL/min secondary).

C_4F_7; 69 (75) CF_3: [EI] 447 (1) $C_9F_{17}O$, M − F; 247 (37) C_5F_9O; 219 (43) C_4F_9; 69 (100) CF_3. ^{19}F NMR (1% $CFCl_3/CDCl_3$) ϕ_A −61.61 ppm (t of m), ϕ_B −109.32 (hexadec of doublets), ϕ_C −184.26 (m), ϕ_D −71.82 (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 $C_9F_{18}O$: C, 23.19; F, 73.37. Found: C, 22.33; F, 71.16.

1-Fluoro-2,2,4,4-tetramethyl-3-pentanone, $(CH_3^A)_3CC(O)C(CH_2^BF^C)(CH_3^D)_2$: 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 [m/e (relative intensity) formula]: [CI] 161 (4) $C_9H_{18}OF$, M + H; 103 (28) C_5H_8OF; 101 (46) C_5H_6OF; 59 (100) C_2FO: [EI] 69 (30) C_5H_9; 57 (23) C_4H_9; 44 (71) C_2H_4O; 32 (100) CH_2F. ^{19}F NMR (1% $CFCl_3/CDCl_3$/0.2% $CHCl_3$) ϕ_C −221.76 ppm (t); ^1H NMR δ_A +1.24 ppm (s), δ_B = +4.40 (d), δ_D +1.29 ppm (s); J_{CH_2F} = 47.4 Hz.

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Registry No. 3,3-Dimethyl-2-butanone, 75-97-8; 2,2,4,4-tetramethyl-3-pentanone, 815-24-7; *F*-3,3-dimethyl-2-butanone, 88995-83-9; 3-(difluoromethyl)-*F*-3-methyl-2-butanone, 88995-84-0; 3,3-bis(difluoromethyl)-*F*-2-butanone, 88995-85-1; *F*-2,2,5-trimethyl-3-hexanone, 88995-86-2; 1-fluoro-2,2,4,4-tetramethyl-3-pentanone, 88995-87-3.

Isotriquinacene

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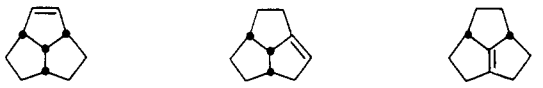
Recent activity at the theoretical level by McKervey[2] as well as Schleyer[3] and at the experimental level by deMeijere[4] has called attention to the strain relationships between the three all-cis tricyclo[5.2.1.$0^{4,10}$]decenes. The energetic costs associated with positioning the double bond at a bridgehead location as in **2** or a double bridgehead site as in **3** are 4.1 and 16.3 kcal/mol, respectively, relative to **1**.



1 **2** **3**

This ordering of stabilities holds particular fascination in the area of triquinacene chemistry where the only tricyclo[5.2.1.$0^{4,10}$]decatriene reported to date, viz. triquinacene (**4**),[5-9] is unique in having no bridgehead double

4 **5** **6**

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