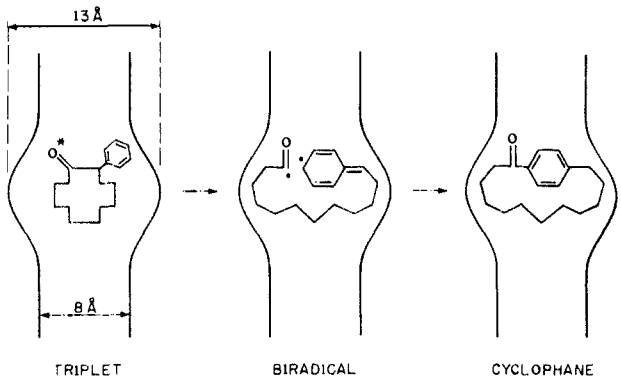

Figure 1. Ship in bottle strategy for encapsulation in a zeolite supercage. The cyclanone K_{12} is cleaved photochemically to the biradical B_{12} and then cyclizes to the cyclophane C_{12}. All of these processes occur within the NaX zeolite supercage. The size/shape of C_{12} prevents its escape from the supercage.

be made to occur entirely within a super cage, the ship in bottle strategy could achieve irreversible encapsulation of C_n in the internal surface of the zeolite.

To test for the experimental realization of this strategy, K_{12} was adsorbed into the internal super cages of NaX zeolite by conventional deposition from pentane solvent.[15] Before photolysis, K_{12} could be reversibly extracted from the zeolite. Photolysis reduced the yield of extractable K_{12}, and C_{12} was not observed in the extracts. However, it was found that C_{12} is produced by photolysis of K_{12} adsorbed on NaX, since dissolution of the entire zeolite framework with HCl followed by neutralization with NaOH and ether extraction resulted in a good yield (ca. 80%) of C_{12}. Since C_{12} is not absorbed into NaX under our reaction conditions, but K_{12} is, the ship in bottle strategy proved successful (Figure 1); i.e., a reactant (K_{12}) whose size and shape allow passage through the pores leading to the NaX super cage is converted photochemically into a product whose size and shape prevent exit from the super cage. Similar results were observed for K_{10}, K_{11}, and K_{15}.

From molecular models a variation of the ship in bottle strategy is apparent for the K_{15}/C_{15} system. This strategy, termed reptation, involves formation of a biradical from photolysis of a cyclanone that is too large to enter the zeolite framework. The biradical, although formed on the external surface, can enter the internal surface by a slithering motion, or reptation, through the pore leading to a super cage. Once inside a super cage, cyclization to a cyclophane causes encapsulation within the super cage. Empirically, it was found that neither the ketone, K_{15}, nor the cyclophane, C_{15}, is adsorbed through the pores of CaX, the Ca^{2+} exchanged form of NaX. However, it is expected that B_{15}, produced by photolysis, can reptate through the zeolite pore and enter the super cage. The process $K_{15}(out) \rightarrow B_{15}(out) \rightarrow B_{15}(in) \rightarrow C_{15}(in)$ would encapsulate the cyclophane internally. This expectation was realized experimentally. After deposition from pentane and drying, >90% of the adsorbed K_{15} and C_{15} were rapidly extracted from CaX with chloroform,[15] indicating little adsorption of either molecule on the internal surface. Upon photolysis of adsorbed K_{15}, however, C_{15} is formed and encapsulated internally as evidenced by the failure of normal extraction to remove C_{15} from the zeolite and the requirement to dissolve the entire zeolite framework in order to release and extract the cyclophane (80% yield).

Acknowledgment. N.J.T. thanks the NSF and DOE for support of this research. C.E.D. thanks NSF (CHE-8421140) for support. Dr. N. Herron of the E. I. du Pont de Nemours and Co. is thanked for a discussion and examples of the the ship in bottle strategy for zeolite systems.

(15) NaX molecular sieves were obtained from Union Carbide (Type 13x powder, lot no. 945083020004-S-1) and heated at 500 °C for 1 h immediately before use. The ketones were adsorbed onto the zeolites from pentane solutions (ca. 1% ketone wt/wt). The pentane was removed by evaporation followed by 12 h at 10^{-3} torr. The samples were maintained under vacuum and tumbled during photolysis (313 nm) at ambient temperature. When K_n or C_n is deposited on NaX zeolite followed by extraction with $CHCl_3$, the amount recovered depends strongly on the time (0.5–12 h) under vacuum during drying after deposition and on the soaking time (0.5–12 h) during the $CHCl_3$ extraction. Shorter drying time or longer soaking time yields a higher percent recovery. However, when K_n or C_n is deposited on 4A zeolite (4-Å openings), all or nearly all the material is recovered after $CHCl_3$ extraction and the percent recovery is *independent* of the drying or soaking time. Since no adsorption inside the zeolite is possible with 4A, the difference is presumably due to adsorption *inside* the NaX super cage structure.

Stereospecific Synthesis of Alkenyl Fluorides (with Retention) via Organometallic Intermediates

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Fluoroorganics are of demonstrated importance in organic chemistry because of their use as medicinals, as tools in medical diagnosis, and in fundamental studies of biochemical and metabolic processes.[1] Consequently, the development of methodology for the specific introduction of fluorine into a variety of types of organic substrates remains a field of active endeavor. Unfortunately, many of the procedures that have been developed for this purpose employ highly reactive and often corrosive materials such as F_2,[2] XeF_2,[3] $FClO_3$,[4] CF_3OF,[5] CH_3COOF,[6] or fluoroamine derivatives.[7] As well, although many routes are available for the creation of fluoro*alkanes*, synthetic methodology for the synthesis of fluoro*alkenes* has not been as well studied;[8] in particular, methods for the *stereospecific* preparation of alkenyl fluorides have not been realized heretofore.[8] Cleavage reactions of alkenylmetallics such as alkenylmercurials,[9] alkenylaluminums,[10] alkenylboranes,[11] or alkenylzirconiums[12] using "positive" halogen reagents have been shown to be of use for the preparation of alkenyl chlorides, bromides, or iodides. However, analogous

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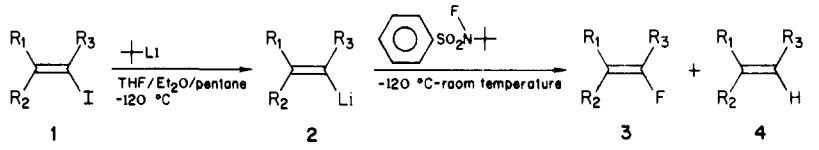
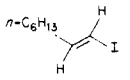
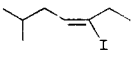
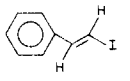
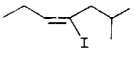
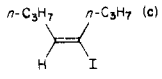
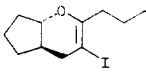
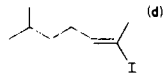
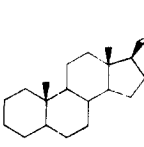
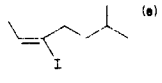
Table I



1 2 3 4

alkenyl iodide	products[d]	alkenyl iodide	products[d]
 (a)	**3**, 71%;[a] **4**, 15% ^{1}H NMR ($CDCl_3$) δ 6.48 ($^2J_{HF}$ = 86.2, $^3J_{HH}$ = 11.0 Hz), 5.33 ($^3J_{HF}$ = 19.1, $^3J_{HH}$ = 11.2, $^3J_{HH}$ = 7.8 Hz) ^{19}F NMR ($CDCl_3$) δ −131.0 $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 148.5 ($^1J_{CF}$ = 253.2 Hz), 111.6 ($^2J_{CF}$ = 8.1 Hz) *m/e* 130 (M^+)	 (f)	**3**, 88%; **4**, 7% ^{1}H NMR ($CDCl_3$) δ 4.94 ($^3J_{HF}$ = 22.5, $^3J_{HH}$ = 8.1 Hz) ^{19}F NMR ($CDCl_3$) δ −106.2 $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 161.8 ($^1J_{CF}$ = 246.2 Hz), 103.3 ($^2J_{CF}$ = 22.1 Hz) *m/e* 130 (M^+)
 (b)	**3**, 76%; **4**, 10% ^{1}H NMR (C_6D_6) δ 6.71 ($^2J_{HF}$ = 83.2, $^3J_{HH}$ = 11.4 Hz), 6.16 ($^3J_{HF}$ = 19.4, $^3J_{HH}$ = 11.4 Hz) ^{19}F NMR ($CDCl_3$) δ −129.8 $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ 150.1 ($^1J_{CF}$ = 259.3 Hz), 113.9 ($^2J_{CF}$ = 15.4 Hz) exact mass calcd 122.0532, found 122.0530 ± 0.0012	 (g)	**3**, 83%; **4**, 7% ^{1}H NMR ($CDCl_3$) δ 5.02 ($^3J_{HF}$ = 22.4, $^3J_{HH}$ = 7.9 Hz) ^{19}F NMR ($CDCl_3$) δ −103.6 $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 159.1 ($^1J_{CF}$ = 245.7 Hz), 108.1 ($^2J_{CF}$ = 21.5 Hz) *m/e* 130 (M^+)
 (c)	**3**, 85%; **4**, 3% ^{1}H NMR ($CDCl_3$) δ 4.99 ($^3J_{HF}$ = 22.4, $^3J_{HH}$ = 7.9 Hz) ^{19}F NMR ($CDCl_3$) δ −105.0 exact mass calcd 130.1158, found 130.1151 ± 0.0013 $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 160.1 ($^1J_{CF}$ = 246.2 Hz), 105.5 ($^2J_{CF}$ = 22.1 Hz)	 (h)	**3**, 74%; **4**, 8% ^{1}H NMR ($CDCl_3$)[b] δ 3.49 ($^3J_{HH}$ = 10.4, $^3J_{HH}$ = 7.3 Hz, 1 H), 2.43–1.09 (m, 15 H), 0.88 ($^3J_{HH}$ = 7.2 Hz, 3 H) ^{19}F NMR ($CDCl_3$) δ −151.0 $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 143.2 ($^1J_{CF}$ = 234.3 Hz), 141.7 ($^2J_{CF}$ = 34.5 Hz) *m/e* 198 (M^+)
 (d)	**3**, 75%; **4**, 12% ^{1}H NMR ($CDCl_3$) δ 5.1–4.9 (m) [C(1) CH_3 δ 1.85 ($^3J_{HF}$ = 17.5, $^4J_{HH}$ = 0.7 Hz)] ^{19}F NMR ($CDCl_3$) δ −96.9 $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.6 ($^1J_{CF}$ = 242.4 Hz), 105.6 ($^2J_{CF}$ = 21.0 Hz) *m/e* 130 (M^+)	 (i)	**3**, 80%;[c] **4**, 13% ^{1}H NMR ($CDCl_3$) δ 6.41 ($^2J_{HF}$ = 86.6, $^3J_{HH}$ = 11.0 Hz), 5.27 ($^3J_{HF}$ = 19.8, $^3J_{HH}$ = 11.0, $^3J_{HH}$ = 8.8 Hz) ^{19}F NMR ($CDCl_3$) δ −129.7 $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 148.1 ($^1J_{CF}$ = 254.4 Hz), 112.5 ($^2J_{CF}$ = 7.9 Hz) *m/e* 304 (M^+)
 (e)	**3**, 75%; **4**, 12% ^{1}H NMR ($CDCl_3$) δ 5.1–4.9 (m) [C(4) CH_2 δ 2.19 ($^3J_{HF}$ = 23.0 Hz)] ^{19}F NMR ($CDCl_3$) δ −104.9 $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 160.9 ($^1J_{CF}$ = 244.8 Hz), 99.3 ($^2J_{CF}$ = 24.7 Hz) *m/e* 130 (M^+)		

[a] All yields were determined by GC except where noted. [b] All protons in compound reported. [c] Isolated (recrystallized) yield. [d] NMR for alkenyl group only, except where indicated.

attempts using electrophilic fluorinating agents have failed.[13] We now find that these other alkenyl halides, especially the iodides, can serve as starting materials for the preparation of the desired fluorides by a convenient method which proceeds both stereo- and regiospecifically.

The reaction between a variety of enolates or alkyl or aryl organometallics and *N*-fluoro-*N*-alkylsulfonamides has been shown to give the corresponding fluorinated derivative in good yield.[14] We find that alkenyllithium reagents, which can be prepared regio- and stereospecifically from the corresponding iodides by metal–halogen exchange,[15] can react at low temperature with a soluble *N*-fluoro-*N*-alkylsulfonamide to give the desired alkenyl fluoride in high yield. In a typical reaction procedure, 2.0 mmol (1.18 mL, 1.7 M solution) of *tert*-butyllithium in pentane was added to 1.0 mmol (238 mg) of alkenyl iodide **1a** in 9 mL of "Trapp"[16] solvent mixture (THF/Et_2O/*n*-pentane = 4:1:1) under argon at −120 °C. The reaction mixture was stirred for 20 min at −120 °C and 1.5 mmol (347 mg) of *N*-*tert*-butyl-*N*-fluorobenzenesulfonamide[17] was added via syringe to the reaction mixture at −120 °C (this compound is preferable to the known tolylsulfonamide derivatives[14] because of its advantageous solubility properties at low temperature). The reaction mixture was kept at −120 °C for 20 min and was then allowed to rise slowly to room temperature. Products were separated by reduced-pressure distillation from the reaction mixture and were purified by preparative GC (see Table I). In a similar manner, **1i**[18] could be converted[19] to **3i** which was purified by flash column chromatography (silica gel, Merck; hexane eluent) and crystallized from hexane (80% yield, >99% purity by GC analysis). We note that reactions run above −120 °C or in pure ether or THF give a higher yield of protonated product relative to the desired fluoroalkene, as does the use of

(13) We have noted that treatment of an alkenylmercurial with an alkyllithium followed by an electrophilic fluorinating agent gives some fluoroalkene, however, in only very low yield.
(14) Barnette, W. E. *J. Am. Chem. Soc.* **1984**, *106*, 452.
(15) Neumann, H.; Seebach, D. *Tetrahedron Lett.* **1976**, *52*, 4839.
(16) Köbrich, G.; Trapp, H. *Chem. Ber.* **1966**, *99*, 680.

(17) This compound was prepared[14] from the corresponding aniline; ^{1}H NMR ($CDCl_3$) δ 7.99–7.51 (m, 5 H), 1.45 (d, *J* = 1.8 Hz, 9 H); $^{13}C\{^1H\}$ 137.5, 133.8, 128.7, 128.6, 66.1 (d, *J* = 12.2 Hz), 26.8 (d, *J* = 6.1 Hz); ^{19}F −62.22. Exact mass. Calcd: 231.0729. Found: 231.0717 ± 0.0023.
(18) The iodide was prepared from the corresponding acetylene for which synthesis, see: Pouzar, V.; Vašíčková, S.; Drašar, P.: Cerný, I.; Havel, M. *Collect. Czech. Chem. Commun.* **1983**, *48*, 2423.
(19) *tert*-Butyllithium (20.0 mmol; 11.8 mL, 1.7 M in pentane); 10.0 mmol (4.12 g) of alkenyl iodide **1i** in 120 mL of Trapp solvent mixture; 15 mmol (3.47 g) of *N*-*tert*-butyl-*N*-fluorobenzenesulfonamide in 10 mL of *n*-pentane. Yield: **3i**, 2.43 g (80%), (purity >99%); mp 80–81 °C; **4i** (0.37 g (13%)). Anal. for $C_{21}H_{33}F$: C, H, F.

sulfonamides containing primary alkyl substituents. As shown in the table, the β-alkoxy-substituted lithium reagent **2h** can be successfully prepared and trapped, without undergoing loss of Li alkoxide, to give fluoroalkene **3h** under these reaction conditions. We are continuing to explore the scope of this procedure with regard to the preparation of other fluorine-substituted enol ethers.

Acknowledgment. We acknowledge support for this work given by the National Institutes of Health.

Registry No. 1a, 42599-17-7; **1b**, 42599-24-6; **1c**, 81793-05-7; **1d**, 101166-41-0; **1e**, 101166-42-1; **1f**, 101166-43-2; **1g**, 101166-44-3; **1h**, 83114-95-8; **1i**, 101198-43-0; **3a**, 32814-17-8; **3b**, 20405-77-0; **3c**, 101166-45-4; **3d**, 101166-46-5; **3e**, 101166-47-6; **3f**, 101198-44-1; **3g**, 101166-48-7; **3h**, 101166-49-8; **3i**, 101198-45-2; $C_6H_5SO_2N(F)C(CH_3)_3$, 101166-50-1.

Laser Desorption Fourier Transform Mass Spectrometry of Chlorophyll *a* and Chlorophyll *b*

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The mass spectral fragmentation behavior of chlorophyll *a* (Chl *a*) was the subject of several recent reports which concluded that intact molecular ions are metastable, with lifetimes on the microsecond time scale.[1-3] Chait and Field,[1,2] using ^{252}Cf fission fragment ionization coupled with a time-of-flight (TOF) mass spectrometer, concluded >99% of molecular ions undergo unimolecular decomposition in less than 67 μs. Tabet et al. reached similar conclusions in their TOF analysis of CO_2 laser desorption of Chl *a*.[3] These studies have serious implications regarding the applicability of laser-desorption Fourier transform mass spectrometry (LD-FTMS), with its inherently longer measurement time scale (>10 ms), to the study of large labile moelcules. Thus, the present study was undertaken to determine whether it would prove possible to observe such species by LD-FTMS.

Positive ion LD mass spectra of Chl *a* and chlorophyll *b* (Chl *b*)[4] were obtained by using a Nicolet FTMS 1000 mass spectrometer which was described previously.[5] Samples were prepared by evaporation of methanol solutions containing approximately 100 μg of Chl *a* or *b* onto a 12.7-mm diameter circular stainless steel direct insertion probe tip. For doped samples, an equal amount of KBr was added to the solution. Each spectrum was obtained from a single CO_2 laser pulse which was focused onto an area of ca. 1 mm^2 on the probe tip. Ions thus produced were trapped by using 1-V trapping potentials for 1.5–2.0 s while desorbed neutrals were pumped away. For improved mass resolution in the spectra presented, a low mass cutoff of 450 amu (100 KHz) was employed. Other measurements revealed few fragment ions at lower masses.

Figure 1 is the high mass region of the mass spectrum of KBr-doped Chl *a*. All four major ions are potassium attachment ions, with the intact molecular ion species (*m/z* 931) clearly predominant. Other ions at *m/z* 653 $[M + K - (phytyl - H)]^+$, *m/z* 621 $[M + K - phytyl - OCH_3]^+$, and *m/z* 577 $[M + K - phytyl - OCH_3 - CO_2]^+$ correspond to simple fragmentations similar to those previously observed. However, these results

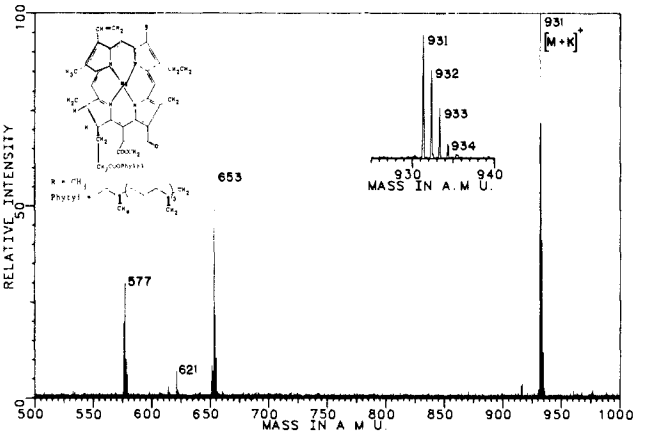

Figure 1. Laser desorption FTMS spectrum of chlorophyll *a* doped with KBr.

Table I. Mass Spectrum of Chlorophyll *b* (doped with KBr)

nominal mass	rel ion intensity	proposed ion struct
945.6	99.3	$[M + K]^+$
667.2	52.4	$[(M + K - (phytyl - H)]^+$
663.6	47.4	*a*
635.6	33.1	$[M + K - phytyl - OCH_3]^+$
628.3	20.6	$[M - (phytyl-H)]^+$
625.5	25.0	*a*
609.5	100.0	$[M + K - CHCOOphytyl]^+$
593.5	13.3	*a*
590.2	14.9	*a*
569.3	8.4	$[M - CH_2COOphytyl]^+$

[a] Not assigned.

Table II. Mass Spectrum of Chlorophyll *b* (no dopant)

nominal mass	rel ion intensity	proposed ion struct
945.5	5.0	$[M + K]^+$
929.5	3.5	$[M + Na]^+$
907.5	11.7	$[M + H]^+$
906.5	9.0	$[M]^+$
651.2	5.8	$[M - (phytyl - H) + Na]^+$
628.2	100.0	$[M - (phytyl - H)]^+$
597.2	16.8	$[M - (phytyl - H) - OCH_3]^+$
596.2	11.6	$[M - phytyl - OCH_3]^+$
575.2	7.9	$[M - (phytyl - H) - OCH_3 - Mg + H_2]^+$
574.2	5.9	$[M - phytyl - OCH_3 - Mg + H_2]^+$
569.2	33.4	$[M - CH_2COOphytyl]^+$
553.2	8.7	$[M - (phytyl-H) - OCH_3 - CO_2]^+$
552.2	8.8	$[M - phytyl - OCH_3 - CO_2]^+$
541.2	7.4	$[M - CH_2COOphytyl - CO]^+$
495.1	18.7	$[M - CHO - COOphytyl - COOCH_3]^+$
481.2	21.9	$[M - CHO - CH_2COOphytyl - COOCH_3]^+$
467.1	8.4	$[M - CHO - CH_2CH_2COOphytyl - COOCH_3]^+$

contrast with the spectra obtained in the earlier LD-TOF study which showed similar dominant alkali attachment ions (Na^+, K^+, and Li^+) but significantly more fragmentation.[3] These differences probably arise primarily from the much different experimental time scale of the LD-TOF and LD-FTMS measurements, as well as the higher laser power densities in the LD-TOF work.

A plausible explanation for the long-term stability of potassium-attached molecular ions in the LD-FTMS experiment regime is their possible formation by relatively slow, low-energy chemical ionization processes during and following the desorption of neutral molecules. Tables I and II summarize the positive ion spectra of Chl *b* with and without KBr dopant. Of particular significance is the observation that fragmentation is much more evident in the spectrum of undoped Chl *b*. However, the presence of molecular ion $[M]^+$ in 9% relative abundance and $[M + H]^+$ at about 6% relative abundance (after correcting for ^{13}C contributions) demonstrates that alkali attachment is not necessary for observation of Chl *b* molecular ions under LD-FTMS conditions. Sodium

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(4) Samples of chlorophyll *a* and chlorophyll *b* were obtained from the Sigma Chemical Co., St. Louis, MO.
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