bontetrachloride in one portion. The resulting mixture was heated for 15 min at reflux temperature. After being cooled to room temperature the solvent was evaporated. The oily residue was crystallized from 15 mL of CH_2Cl_2/CCl_4 (1:4) to give the pentabromide 4 (600 mg). The residue was left 1 day at room temperature, and 7 was crystallized (170 mg). The solvent was removed under reduced pressure, and the oily residue (1900 mg) was chromatographed on silica gel (140 g) eluting with *n*-hexane. After collection of 2.8 L of eluate, the solvent was changed to $CHCl_3$/*n*-hexane (1:5) and elution was continued (4 L of eluate was collected). 4, 6, and 8 were obtained as pure compounds. 7 was obtained as a mixture with 5. This mixture was separated by fractional crystallization from chloroform/*n*-hexane. In the following elution order we obtained 4, 5, 7, 6, and 8.

For 4: 684 mg, 36%; mp 175–176 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 3000, 2990, 1480, 1460, 1280, 1190, 1110, 935, 850; MS *m/e* 549/551/553/555/557/559 (M^+), 469/471/473/475/477 (M – Br), 389/391/393/395 (M – 2Br). Anal. Calcd for $C_{12}H_9Br_5$: C, 26.08; H, 1.64. Found: C, 26.02; H, 1.59.

For 5: 170 mg, 9%; IR (KBr, cm^{-1}) 2920, 1480, 1460, 1240, 1210, 1200, 935, 650. Anal. Calcd for $C_{12}H_9Br_5$: C, 26.08; H, 1.64. Found: C, 26.42; H, 1.55.

For 7: 342 mg, 18%; mp 180 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 2980, 1480, 1460, 1260, 1210, 1100, 935, 885; MS *m/e* 549/551/553/555/557/559 (M^+), 469/471/473/475/477 (M – Br). Anal. Calcd for $C_{12}H_9Br_5$: C, 26.08; H, 1.64; Br, 72.28. Found: C, 25.97; H, 1.51.

For 6: 95 mg, 5%; IR (KBr, cm^{-1}) 3040, 2970, 1460, 1260, 1190, 1100, 975, 935, 860. Anal. Calcd for $C_{12}H_9Br_5$: C, 26.08; H, 1.64; Br, 72.28. Found: C, 26.35; H, 1.53.

For 8: 133 mg, 7%; mp 171 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 2960, 1480, 1460, 1330, 1290, 1240, 1200, 1190, 1110, 930; MS *m/e* 549/551/553/555/557/559 (M^+), 469/471/473/475/477 (M – Br) 389/391/393/395 (M – 2Br). Anal. Calcd for $C_{12}H_9Br_5$: C, 26.08; H, 1.64; Found: C, 25.92; H, 1.54.

General Procedure for Bromination of 9–12. To a solution of 40 mg (0.1 mmol) of tribromide in 1 mL of chloroform was added a solution of 20 mg (0.1 mmol) of bromine in 1 mL of chloroform at room temperature, and the resulting mixture was stirred. Bromination of 9 and 10 was completed in 1.5 h and bromination of 11 and 12 in 0.5 h. 4 and 7 were formed nearly in quantitative yield. Reaction of 9 and 12 with bromine resulted in the formation 5 and 6 in a ratio of 2:1 and 4 and 8 in a ratio of 53:47, respectively.

General Procedure for Dehydrobromination of 4 and 7. To a solution of 56 mg (0.1 mmol) sodium methoxide in 15 mL of dry and freshly distilled THF was added 553 mg (0.1 mmol) of pentabromide 4 or 7. The resulting reaction mixture was refluxed for 3 h. After being cooled to room temperature the solution was poured into a mixture of hexane (40 mL) and water (40 mL). The layers were separated, and the aqueous phase was extracted with hexane. The combined organic layers were washed with water (2 × 40 mL), dried, and evaporated. The residue was purified by filtration through a short silica gel (5 g) column. Elution with hexane and crystallization from chloroform/hexane gave tetrabromides 13 and 14.

For 13: 425 mg, 90%. Anal. Calcd for $C_{12}H_8Br_4$: C, 30.55; H, 1.71. Found: C, 30.22; H, 1.59.

For 14: 448 mg, 95%; mp 210–212 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 3000, 1605, 1460, 1455, 1235, 1220. Anal. Calcd for $C_{12}H_8Br_4$: C, 30.55; H, 1.71. Found: C, 30.29; H, 1.61.

2,3,5-Tribromobenzobarrelene (15). To a magnetically stirred solution of 1106 mg (2 mmol) of a mixture consisting of 4–8 (obtained by bromination of 1 at high temperature) in 30 mL of dry and freshly distilled THF was added a solution 450 mg (4 mmol) of potasium *tert*-butoxide in 15 mL of THF. The resulting reaction mixture was refluxed for 3 h. After being cooled to room temperature, the solution was poured into a mixture of hexane (50 mL) and water (50 mL). The organic phase was washed with water, dried, and rotoevaporated. The residue was chromatographed on silica gel (25 g). Elution with petroleum ether and crystallization from methylene chloride/pentane gave tribromide 2.

For 2: 545 mg, 70%; mp 178–179 °C; IR (KBr, cm^{-1}) 3020, 1610, 1455. Anal. Calcd for $C_{12}H_7Br_3$: C, 36.87; H, 1.86; Br, 61.32. Found: C, 36.39; H, 1.81.

Bromination of 2. To a magnetically stirred solution of 1564 mg (4 mmol) of 2,3,5-tribromobenzobarrelene 2 in 25 mL of carbon tetrachloride was added a solution of 440 mg (4.1 mmol) of bromine in 10 mL of carbon tetrachloride at room temperature. The resulting solution was stirred for 45 min. NMR studies indicated the formation of the isomers 15 and 16 in a ratio of 48:52 in quantitative yield. The solvent was evaporated, and products were separated by fractional crystallization from chloroform/*n*-hexane.

For 15: mp 183–184 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 2990, 2980, 1600, 1475, 1460, 1150, 1100, 1090, 1030, 990, 960.

For 16: mp 153–154 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 1615, 1600, 1475, 1315, 1250, 1195, 1080, 1025, 970; MS *m/e* 547/549/551/553 (M^+), 469/471/473 (M – Br), 388/390/392/394 (M – 2Br), 284)286/288 (M – 3Br, –2C).

Synthesis of 3. To a magnetically stirred solution of 1102 mg (2 mmol) of a mixture consisting of 15 and 16 (obtained by bromination of 2) in 30 mL of dry and freshly distilled THF was added a solution of 235 mg (2.1 mmol) of potasium *tert*-butoxide in 10 mL of THF. The resulting reaction mixture was refluxed for 3 h. After being cooled to room temperature, the solution was poured into a mixture of hexane (50 mL) and water (50 mL). The organic phase was washed with water, dried, and rotoevaporated. The residue was chromatographed on silica gel (10 g). Elution with carbontetrachloride and crystallization from chloroform/carbontetrachloride gave the tetrabromide 3.

For 3: 844 mg, 90%; mp 208–210 °C; IR (KBr, cm^{-1}) 3080, 3020, 1590, 1460, 1450, 1190, 1140, 1060, 980, 850; MS *m/e* 466/468/470/472/474 (M^+), 387/389/391/393 (M – Br), 308/310/312 (M – 2Br). Anal. Calcd for $C_{12}H_6Br_4$: C, 30.71; H, 1.29; Br, 68.11. Found: C, 30.49; H, 1.34.

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Registry No. 1, 55277-75-3; 2, 143969-91-9; 3, 143969-92-0; 4, 144068-58-6; 5, 144068-59-7; 6, 144068-60-0; 7, 144068-61-1; 8, 144068-62-2; 9, 129196-78-7; 10, 129262-09-5; 11, 129262-10-8; 12, 129196-79-8; 13, 144000-18-0; 14, 144070-28-0; 15, 144000-19-1; 16, 144070-29-1.

Addition of Fluorinated Olefins to Ester Enolates. Synthesis of Fluorinated Carboxylic Esters and Tetrafluorocyclobutanes

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Introduction

Use of polyhalogenated olefins for the incorporation of fluorine into organic molecules and numerous reactions involving their use as either nucleophilic and electrophilic synthons have been described. In particular, nucleophilic additions to fluorinated olefins by aryl,[1] alkyl,[2] and allyl[3] anions, as well as sulfur and other nucleophiles,[4] have been reported. In addition, lithiotrifluoroethylene,[5] 1-lithio-2,2-difluoroethylene,[6] and 1-lithio-1-chloro-2,2-difluoro-

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Table I. Composition of Volatile Products Arising from Addition of Ethyl α-Lithioisobutyrate (1) to Polyhaloolefins

olefin	product distribution (% isolated yield) unsaturated ester(s)	saturated ester	cyclobutyl hemiketal
CH_2=CF_2	58	0	0
CH_2=CCl_2	0	8	0
CHF=CF_2	43[a]	3.5	0
CF_2=CF_2	18	0	8
CF_2=$CFCF_3$	52[b]	0	0
CF_2=CFCl	54[c]	0	0

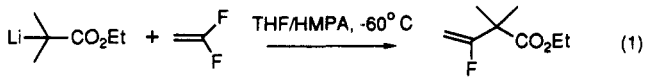
[a] E:Z isomer ratio 5:1. [b] E isomer only. [c] E:Z isomer ratio 1:9.

ethylene[7] have been used in nucleophilic additions to aldehydes, ketones, acid chlorides, and carbon dioxide, as well as in substitutions involving alkyl halides. In general, reaction of polyfluoroolefins with nonstabilized alkyllithium compounds can result in either addition, deprotonation, or metalation products, depending on the particular olefin used and on the basicity and steric bulk of the nucleophile. The resultant anion can than undergo elimination or protonation.

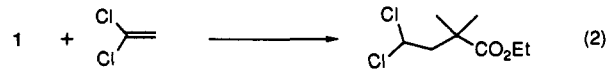
In connection with the preparation of a series of carboxanilides containing haloolefin side chains as potential herbicides,[8] we were interested in examining the interaction of perfluoroolefins with less basic carbon nucleophiles, such as enolates. Kende et al. have described additions of various carbanions to polychloroolefins;[9] these molecules in general react poorly with ester enolates. A report by Kende concluded that 1,1,2-trifluoroethylene was essentially unreactive toward ester lithium enolates in THF/HMPA, and that a stronger base, *sec*-butyllithium, was necessary in order to form the (presumably) more reactive difluoroethylene.[10] No other enolate additions to polyfluorinated olefins have been reported.

Results

We undertook an examination of reactions of this type, using ethyl α-lithioisobutyrate (1) as a representative nucleophile. We have found that reaction of 1 with a variety of polyfluoroolefins yields products arising from nucleophilic addition at the carbon bearing the greatest number of fluorine atoms. Thus, reaction of 1 with 1,1-difluoroethylene (2) at −60 °C in THF containing 1 equiv of HMPA gave the 3-fluoro-3-butenoate derivative 3 in 58% isolated yield (eq 1). The addition was opposite in orientation to and was much higher yielding than enolate addition to 1,1-dichloroethylene (4), which under identical conditions delivered the 4,4-dichlorobutyrate ester 5 (5–10% isolated yield) as the only volatile product (eq 2).

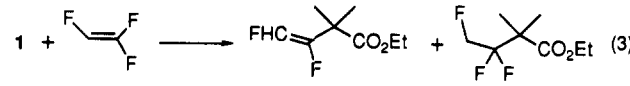


1 2 3 (1)



4 5 (2)

Reaction with other haloolefins resulted in formation of a variety of products; all, however, can be envisioned as arising from initial Michael addition to the double bond (see Table I). Thus, in contrast to the reported unreactivity of 1 to trifluoroethylene (6),[10] in our hands this reaction generated the *E* and *Z* isomers 7 and 8 (43% isolated yield) in a ratio of 5:1 (eq 3). Stereochemical assignments were made based on observed vinylic H–F coupling constants, the smaller (5.9 Hz) being assigned the *E* configuration and the larger (17.6 Hz) to the *Z* configuration. In addition, a small amount (<5%) of the saturated derivative 9 was also identified in the volatile product mixture (see Experimental Section).



6 7 (E) 8 (Z) 9 (3)

Tetrafluoroethylene (TFE, 10) was also reactive to 1, yielding after careful fractional distillation, two volatile fractions. The major product, boiling at 30–37 °C (5 mmHg), was identified as the expected trifluorovinyl derivative 11 (Scheme I). The minor, lower boiling component, which could not be completely separated from the THF solvent, was identified as the [2 + 2] addition product 12. Specifically, ^{1}H NMR showed an ethoxy ether group, a six-proton methyl singlet, and an exchangeable proton. Both 11 and 12 were further characterized by hydrolysis in ethanolic KOH; 11 formed the expected unsaturated acid 13, and 12 generated the saturated tetrafluoro acid 14. The ^{1}H NMR of 14 displayed a characteristic CF_2CF_2H triplet of triplets (see Experimental Section).

The relative ratio of unsaturated ester to hemiketal could be shifted in favor of the former by utilizing higher reaction temperatures, although in no case could conditions be found which led to exclusive formation of either product.

The low material balance suggested that the volatile hemiketal product, whose boiling point (88–90 °C at ambient pressure) is not much higher than THF, may have been lost on workup. In contrast, a higher molecular weight ester, ethyl cyclohexanecarboxylate, yielded none of the unsaturated ester and only a 3% yield of the spirocyclic hemiketal 15. The majority of the distilled product (57%) was the tetrafluorocyclobutanone 16. The ^{13}C spectrum of 16 displayed two triplets of triplets centered at 117 ppm for the two fluorine-bearing carbons. The further downfield set had 284-Hz geminal and 27-Hz vicinal coupling constants; those for the upfield signal were 309 and 22 Hz, respectively. In addition, both the quaternary and the carbonyl carbons showed long range fluorine coupling, both signals appearing as complex multiplets at 66.5 and 199.9 ppm, respectively.

The hemiketal, stable toward acid, was converted slowly to the ketone on heating. Hence, the observed product ratio is not a reflection of products formed during the reaction, but rather the percent of hemiketal that has been converted to ketone under the conditions of distillation. The crude reaction mixture, by NMR analysis, contains very little ketone 16. Material balance was considerably improved over the isobutyrate example, although the combined yield (60%) still suffered due to concomitant formation of unidentified higher boiling materials.

The ketone reacted exothermically with EtOH, quantitatively regenerating 15. Further treatment of 15 in EtOH with sodium hydroxide resulted in ring cleavage to the tetrafluoro acid 17 (Scheme II).

Hexafluoropropene (HFP, 18) reacted much more cleanly with 1 than did TFE; thus, reaction under similar conditions delivered exclusively the unsaturated ester 19

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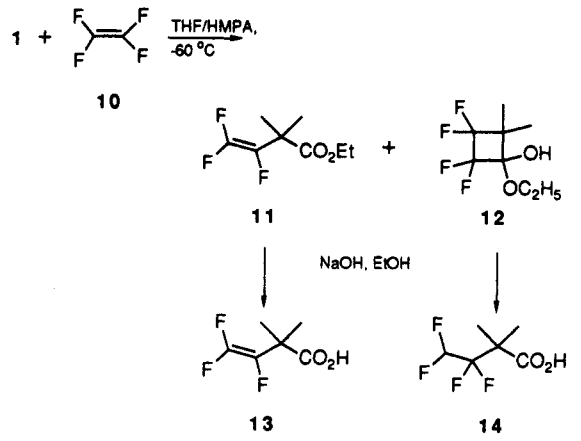
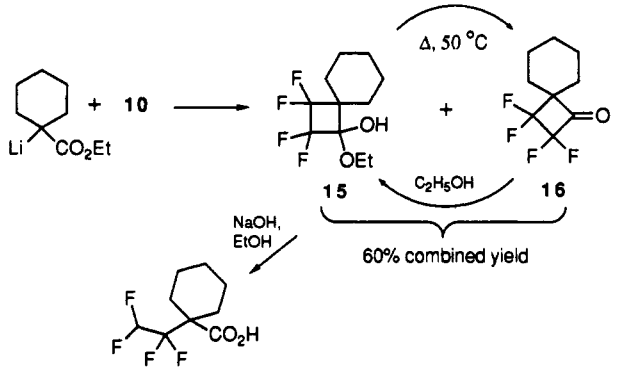
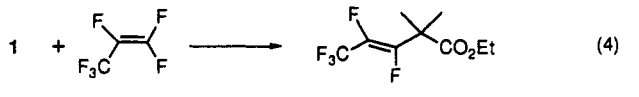
Scheme I

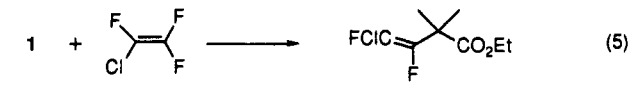


Scheme II



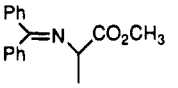
in 52% isolated yield (eq 4). The *E* orientation was confirmed by a 135-Hz coupling constant between the two vinylic fluorines. Similarly, chlorotrifluoroethylene (**20**) yielded *Z* and *E* isomers **21** and **22** (90:10) in moderate yield (eq 5), the larger fluorine coupling constant (129 Hz vs 17 Hz) being assigned to the *Z* isomer in which the two vinylic fluorine atoms are oriented trans to each other. Careful analysis of the crude reaction products of this or the trifluoroethylene addition reaction failed to reveal hemiketal products analogous to **12**.

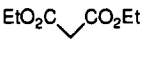




Discussion

In each example above, the isolated products most likely arise through initial nucleophilic addition of the enolate to a polyhalogenated olefin. The regiochemistry of nucleophilic addition to polyfluorinated olefins is generally dictated by the stability of the intermediate anion; thus greater stabilization of the anionic intermediate by β-fluorine atoms dictates that the more highly fluorine-substituted vinylic position is preferentially attacked.[11] Subsequent chemical pathways then diverge to give a variety of end products. The lower basicity of the ester enolate as compared with unstabilized carbon anions is apparently insufficient to deprotonate and/or dehydrohalogenate the olefins prior to nucleophilic attack. Less basic lithium enolates, such as those generated from the diphenylimine of alanine methyl ester (**23**) or diethyl malonate (**24**), afforded no observable addition products with TFE.[12]





The cyclobutyl derivatives **12** and **15** could be envisioned as arising from intramolecular capture of the intermediate difluoromethyl anion by the ester and to our knowledge represent the first examples wherein a difluoroalkyl anion is captured in an intramolecular sense by an electrophile.[13] It is apparently the inherent tendency of carbon α to perfluoroalkyl groups to prefer to remain in the sp^3 hybridization state which stabilizes the hemiketal enough to allow isolation.[14] Other [2 + 2] cycloadditions with TFE are well known;[15] however, these involve high pressures and temperatures and are generally considered to involve a radical mechanism.

Experimental Section

General Information. All reagents used were available commercially and were used without further purification. ^1H and ^{13}C NMR data were obtained on a Bruker 250 MHz or Gemini 300 MHz spectrometer using $CDCl_3$ with TMS internal standard; ^{19}F NMR spectra were obtained on an IBM NR80 spectrometer, using $CDCl_3$ solvent and trichlorofluoromethane internal standard. VPC yields were determined using a Hewlett-Packard gas chromatograph. Melting points are uncorrected. Isolated yields reported herein are not maximized.

Ethyl 3-Fluoro-2,2-dimethyl-2-butenoate (3). Lithium diisopropylamide (LDA, 142 mmol) was prepared by adding *n*-BuLi in hexane (65 mL of 2.2 M, 142 mmol) to a stirred solution of diisopropylamine (14.3 g, 142 mmol) in 200 mL of dry tetrahydrofuran at −50 °C. Ethyl isobutyrate (14.9 g, 129 mmol) was added dropwise, and after addition, the solution was stirred an additional 1 h at −60 °C. Then HMPA (23.1 g, 129 mmol) was added in one portion.

In a separate flask 1,2-dibromo-1,1-difluoroethane (32 g, 142 mmol) was added dropwise to a stirred slurry of powdered zinc (16.9 g, 258 mmol) in 75 mL of absolute ethanol. The resulting gaseous 1,1-difluoroethylene was bubbled through the cold anionic solution above, the temperature rising to −50 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature with stirring over the next 2 h and then poured onto 200 g of crushed ice and 25 mL of concentrated HCl. The product was extracted into 2 × 200 mL of ether, washed with 2 × 200 mL of water, and dried over anhydrous $MgSO_4$. Concentration under vacuum at 0 °C yielded 19 g of a yellow oil. ^1H NMR revealed the product to be largely **3** with some starting ethyl isobutyrate and some THF present. Distillation yielded 12.0 g (58%) of nearly pure **3** as a clear, colorless oil, bp 30–55 °C (25 mmHg). An analytical sample was obtained by subsequent redistillation: bp 146–150 °C (ambient pressure); ^1H NMR (DMSO-d_6) δ 4.95–4.26 (m, 2 H), 4.11 (q, J = 7.1 Hz, 2 H), 1.32 (s, 6 H), 1.17 (t, J = 7.1 Hz, 3 H); ^{19}F NMR (DMSO-d_6) δ −100.4 (dd, J = 19, 52 Hz).

Ethyl 4,4-Dichloro-2,2-dimethylbutanoate (5). To a solution of 1 (100 mmol), prepared in THF/HMPA as described above at −60 °C, was added 1,1-dichloroethylene (25 g, 260 mmol) dropwise over 15 min. The solution was maintained at this

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(12) Crouse, G. D., unpublished results.

(13) Attempts to isolate addition products to $RCFCl^-$ anions have been unsuccessful; see ref 4.

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temperature an additional 45 min and then allowed to warm slowly to ambient temperature. The reaction mixture was worked up as described above to furnish 1.5 g (8%) of **5**: bp 80–85 °C (10 mmHg); ^{1}H NMR ($CDCl_3$) δ 5.9 (t, J = 2.4 Hz, 1 H); 4.1 (q, J = 2.8 Hz, 2 H); 2.6 (d, J = 2.4 Hz, 1 H); 1.3–1.1 (M, 9 H).

Reaction of Trifluoroethylene (6) with Ethyl Lithioisobutyrate: (*E* and *Z*)-Ethyl 3,4-Difluoro-2,2-dimethyl-3-butenoate (7 and 8) and Ethyl 2,2-Dimethyl-3,3,4-trifluorobutanoate (9). A solution of 1 (129 mmol) was prepared in THF/HMPA as described above and kept at −60 °C. In a separate flask, 1,2-dibromo-1,1,2-trifluoroethane (34.4 g, 142 mmol) was added dropwise to a stirred slurry of powdered zinc (16.9 g, 258 mmol) in 75 mL of absolute ethanol. The resulting gaseous 1,1,2-trifluoroethylene was bubbled through the anionic solution at −60 °C. Upon completion of the addition, the mixture was allowed to warm slowly to −15 °C and was then worked up as described above to afford 18.7 g of an oil. Fractional distillation at 10 mmHg gave two fractions. The first (3 g, bp < 30 °C) consisted of THF, unreacted starting material, and a small amount of **7**. The second cut (10.8 g, bp 44–46 °C), consisted of **7**, **8**, and **9** in approximately a 76:16:8 ratio. The ^{1}H NMR of **7** was identical to that reported previously.[10] The *Z* isomer **8** was identified by the vinylic ^{1}H doublet of doublets centered at δ 6.4 (J_{HF} = 17 and 76 Hz) vs δ 7.0 (J_{HF} = 6 and 74 Hz) for the *E* isomer. The saturated ester **9** was identified by a doublet of triplets centered at δ 4.8 (J = 13.5, 43 Hz). The ester mixture was further characterized by hydrolysis to the acids and subsequent formation and chromatographic separation of the corresponding *p*-chloroanilides. Additional spectroscopic data are included in the supplementary material.

Reaction of TFE (10) with Ethyl α-Lithioisobutyrate. Ethyl 2,2-Dimethyl-3,4,4-trifluoro-3-propenoate (11) and 2,2-Dimethyl-3,3,4,4-tetrafluorocyclobutanone, Ethyl Hemiketal (12). A solution of 1 (86 mmol) was prepared as described above and was stirred at −60 °C. In a separate flask, 1,2-dibromo-1,1,2,2-tetrafluoroethane (44.7 g, 172 mmol) was added dropwise to a stirred slurry of powdered zinc (16.9 g, 258 mmol) in 75 mL of absolute ethanol. The resulting gaseous TFE was bubbled through the cold, vigorously stirred anionic solution. Dry ice was added to the cooling bath as needed to maintain the reaction temperature at −60 °C. Upon completion of the addition, the solution was stirred at −60 °C for an additional 2 h and then was worked up as described above, and the solvents were removed at 0 °C. The residual oil was fractionally distilled to furnish 4.4 g of **11**, bp 30–32 °C (100 mmHg), and 3.0 g of **12**, bp 30–37 °C (10 mmHg). The remainder of the crude product was resinous pot residue. Compounds **11** and **12** were each further characterized as the derived acids (**13** and **14**) following hydrolysis with NaOH in EtOH.

For **11**: ^{1}H NMR ($CDCl_3$) δ 4.2 (q, J = 7 Hz, 2 H), 1.45 (br s, 6 H), 1.3 (t, J = 7 Hz, 3 H); ^{19}F NMR ($CDCl_3$) δ −102 (dd, J = 36, 85 Hz, 1 F), −117 (dd, J = 85, 110 Hz, 1 F), −175 (dd, J = 36, 110 Hz, 1 F).

For **12**: ^{1}H NMR ($CDCl_3$) δ 3.6–3.8 (m, 2 H), 3.1 (br s, −OH), 1.3 (t, J = 7 Hz, 3 H), 1.2 (s, 6 H).

3,4,4-Trifluoro-2,2-dimethyl-3-butenoic acid (13): ^{1}H NMR ($CDCl_3$) δ 8.5 (br s, 1 H), 1.5 (m, 6 H); ^{19}F NMR ($CDCl_3$) δ −101 (dd, J = 85, 35 Hz, 1 F), −117 (dd, J = 85, 112 Hz, 1 F), −175 (dd, J = 35, 112 Hz, 1 F).

3,3,4,4-Tetrafluoro-2,2-dimethylbutanoic acid (14): ^{1}H NMR ($CDCl_3$) δ 9.4 (br s, 1 H), 6.2 (tt, J = 5.0, 53 Hz, 1 H), 1.5 (m, 6 H); ^{19}F NMR ($CDCl_3$) δ −123 (br s, 2 F), −134 (br d, J = 53 Hz, 2 F).

Reaction of TFE (10) with Ethyl α-Lithiocyclohexanecarboxylate. 2,2,3,3-Tetrafluorospiro[5.3]nonan-1-one (16). Reaction of 165 mmol of LDA, 150 mmol of ethyl cyclohexanecarboxylate, and 25 g (250 mmol) of TFE following conditions described above yielded 19.6 g (60%) of a colorless oil, bp 29–39 °C (8 mmHg). VPC analysis indicated **15** and **16** were present in a ratio of 5:95.

For **16**: mp 35 °C; bp 35–38 °C (8 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (m, 4 H), 1.7–1.4 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9 (m), 119.39 (tt, J = 309, 27 Hz), 117.62 (tt, J = 22, 284 Hz), 26.3, 25.5, 23.3; ^{19}F NMR ($CDCl_3$) δ −118 (br s, 2 F), −112.6 (br s, 2 F).

Dissolving **16** in ethanol at ambient temperature followed by low temperature (0 °C) evaporation of solvent regenerated the hemiketal **15**, which on attempted distillation was reconverted to the ketone **16**.

For **15**: ^{1}H NMR δ 3.55–3.80 (m, 2 H), 3.2 (br s, 1 H), 1.4–1.85 (m, 10 H), 1.2 (t, J = 8 Hz, 3 H).

Hydrolysis of **16** (or **15**) with 1 equiv of NaOH in ethanol generated the tetrafluoro acid **17**, mp 52 °C; ^{1}H NMR δ 9.2 (br s, 1 H); 6.0 (tt, J = 7, 52 Hz, 1 H); 2.3 (br d, J = 12 Hz, 2 H); 1.2–1.8 (m, 8 H).

Ethyl 2,2-Dimethyl-3,4,5,5,5-pentafluoro-3-pentenoate (19). A solution of 1 (129 mmol) was prepared in THF/HMPA as described above. The anionic solution was stirred at −60 °C, and HFP (18; 58 g, 387 mmol) was bubbled through the cold solution, the temperature rising to −35 °C. The mixture was stirred at −60 °C for an additional 0.5 h and was then worked up under standard conditions. Solvent was removed at ambient pressure. Vacuum distillation of the crude oil yielded 16.5 g of **19** as a colorless oil: bp 38–41 °C (10 mmHg); ^{1}H NMR ($CDCl_3$) δ 4.22 (q, J = 7.1 Hz, 2 H), 1.50 (m, 6 H), 1.27 (t, J = 7.1 Hz, 3 H); ^{19}F NMR ($CDCl_3$) δ −68 (m, 3 F), −144 (dq, J = 23, 134 Hz, 1 F), −171 (dd, J = 12, 134 Hz, 1 F).

(*Z* and *E*)-Ethyl 4-Chloro-3,4-difluoro-2,2-dimethyl-3-butenoate (21 and 22). A solution of 1 (129 mmol) was prepared in THF/HMPA as described above. The anionic solution was stirred at −60 °C, and chlorotrifluoroethylene (26.1 g, 224 mmol) was bubbled through the cold solution, the temperature rising quickly to −20 °C. Addition of the gas was discontinued until the temperature again fell to −60 °C, and then the remainder of the gas was bubbled through without significant rise in temperature. Upon completion of the addition, the mixture was worked up as described above. Solvent was removed at ambient temperature. The crude product was distilled under vacuum to afford 12.7 g of *E*/*Z* isomers **21** and **22**, bp 42–55 °C (10 mmHg). An analytically pure sample was obtained by redistillation, bp 44–49 °C (10.5 g). By ^{19}F NMR analysis the *Z*/*E* ratio is approximately 9:1: ^{1}H NMR ($CDCl_3$) δ 4.17 (q, J = 7.1 Hz, 2 H), 1.50 (m, 6 H), 1.28 (t, J = 7.1 Hz, 3 H); ^{19}F NMR ($CDCl_3$) *Z* isomer δ −121 (d, J = 129 Hz, 1 F), −145 (d, J = 129 Hz, 1 F); *E* isomer δ −105 (d, J = 17 Hz, 1 F), −134 (d, J = 17 Hz, 1 F).

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Registry No. **2**, 75-38-7; **3**, 131399-85-4; **4**, 75-35-4; **5**, 144193-96-4; **6**, 359-11-5; **7**, 85066-79-1; **8**, 131399-90-1; **9**, 144193-97-5; **10**, 116-14-3; **11**, 144193-98-6; **12**, 144193-99-7; **13**, 144194-00-3; **14**, 144194-01-4; **15**, 144194-02-5; **16**, 144194-03-6; **17**, 144194-04-7; **18**, 116-15-4; **19**, 144194-05-8; **20**, 79-38-9; **21**, 144194-06-9; **22**, 144194-07-0; ethyl isobutyrate, 97-62-1; ethyl cyclohexanecarboxylate, 3289-28-9; 1,2-dibromo-1,1-difluoroethane, 75-82-1; 1,2-dibromo-1,1,2-trifluoroethane, 354-04-1; 1,2-dibromo-1,1,2,2-tetrafluoroethane, 124-73-2.

Supplementary Material Available: Elemental analyses of all new compounds and preparation and characterization data of **7**, **8**, and **9** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Surface-Mediated Reactions. 2. Addition of Hydrazoic Acid to Alkenes[1]

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Organic azides are versatile intermediates for organic synthesis.[2] Whereas aromatic azides can be readily ob-

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