Table II. Properties of 3-Arylsydnones-4-*N*-methylcarboxamides (2)[a]

compd	yield,[b] %	mp, °C	mass spectrum (M^+, *m/e*)	IR (KBr), cm^{-1} ν_{N-H}	IR (KBr), cm^{-1} $\nu_{C=O}$	NMR ($CDCl_3$), δ
2a	50	185-186	219	3350	1740	2.86 (d, 3 H)
					1655	7.62 (s, 6 H)
2b	77	228-229	233	3340	1742	2.52 (s, 3 H)
					1660	2.94 (d, 3 H)
						7.42 (m, 5 H)
2c	74	220-222	297	3344	1740	2.78 (d, 3 H)
			299		1660	7.58 (q, 5 H)
2d	58	158-160	249	3344	1746	2.96 (d, 3 H)
					1670	3.94 (s, 3 H)
						7.26 (q, 5 H)
2e	63	163-164	263	3352	1743	1.49 (t, 3 H)
						2.95 (d, 3 H)
					1670	4.16 (q, 2 H)
						7.28 (q, 5 H)

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in the table. [b] After purification.

was slowly added 0.22 g (0.001 mol) of **1a** with stirring. The reaction mixture was heated at 80 °C for 3 h, and after cooling it was poured into crushed ice. Unreacted **1a** (0.11 g) was collected by filtration, and the filtrate, after neutralized with sodium bicarbonate, was extracted with dichloromethane (3 × 30 mL). Additional **1a** (0.03 g) was recovered by evaporating the extract. The overall recovery of **1a** was 0.14 g (64%). In the reaction at temperatures below 70 °C, the starting **1a** was almost quantitatively recovered.

Preparation of 4-Acetyl-3-arylsydnones (4a-e). The 4-acetylsydnones were prepared by a modified method of the literature.[4,5] A typical procedure was as follows: To a well-cooled suspension of 3-phenylsydnone (6.84 g, 0.04 mol) in acetic anhydride (20 mL) in a strongly cooled bath (−15 °C) was added well-cooled solution of 60% perchloric acid (1 mL) in acetic anhydride (20 mL) gradually with stirring. After cooling and stirring the solution for 1 h, the temperature of the reaction mixture was elevated to 12 °C to dissolve completely the starting 3-phenylsydnone, and then the mixture was allowed to stand at room temperature for 2 h. The resulting light-brown solution was poured into ice–water to decompose excess acetic anhydride. Recrystallization of the resulting precipitates from 95% ethanol afforded 5.10 g (63% yield) of pure **4a** as colorless plates.

Schmidt Reaction of 4-Acetyl-3-arylsydnones (4a-e). A typical procedure for the Schmidt reaction of **4** is given below. To an ice-cooled solution of **4a** (1.00 g, 0.0049 mol) in concentrated sulfuric acid (15 mL) and water (5 mL) was added sodium azide (0.40 g, 0.062 mol) in small potions with stirring. After cooling and stirring the solution for 1 h, the cooling bath was removed and stirring was continued at room temperature for 5 h. The reaction mixture was poured into crushed ice, and the crude product (0.5 g) was collected by filtration. By extracting filtrate with benzene (3 × 100 mL) and evaporating the benzene under reduced pressure, more crude product (0.2 g) was obtained. Recrystallization of the combined crude product from 95% ethanol afforded pure **2a** (0.54 g, 50% yield) as colorless needles.

Synthesis of 3-Arylsydnone-4-*N*-methylcarboxamides (2a,b) from 3-Aryl-4-sydnonecarboxylic Acid Chlorides and Methylamine. 3-Phenyl- and 3-*p*-tolyl-4-sydnonecarboxylic acid chlorides were prepared from the corresponding 4-sydnonecarboxylic acids by the method of the literature.[8] To ice-cooled *N,N*-dimethylformamide (15 mL) containing 1 mL (0.013 mol) of 40% methylamine was added 0.22 g (0.001 mol) of 3-phenyl-4-sydnonecarboxylic acid chloride slowly. After cooling for 1 h, the reaction mixture was allowed to stand at room temperature for 3 h and then poured into ice–water. Recrystallization of the resulting precipitates from 95% ethanol afforded 0.16 g (72% yield) of pure **2a** which was identified with the sample obtained in the Schmidt reaction. Similarly, **2b** was synthesized in 83% yield from 3-*p*-tolyl-4-sydnonecarboxylic acid chloride and methylamine.

Acknowledgment. We are grateful for valuable discussions with Dr. T. Fuchigami and thank Mr. C.-S. Chen for doing part of the experiments.

Registry No. **1a**, 13973-41-6; **2a**, 84877-58-7; **2b**, 84877-59-8; **2c**, 84877-60-1; **2d**, 84877-61-2; **2e**, 84877-62-3; **4a**, 13973-33-6; **4b**, 72913-08-7; **4c**, 84877-63-4; **4d**, 34356-36-0; **4e**, 63935-02-4; 4-acetyl-3-phenylsydnone oxime *O*-acetate, 84877-64-5; 3-phenylsydnone, 120-06-9; acetic anhydride, 108-24-7; 3-phenyl-4-sydnonecarboxylic acid chloride, 21074-30-6; 3-*p*-tolyl-4-sydnonecarboxylic acid chloride, 21074-35-1; methylamine, 74-89-5; 3-(4-bromophenyl)sydnone, 26537-61-1; 3-(4-methoxyphenyl)sydnone, 3815-80-3; 3-(4-ethoxyphenyl)sydnone, 3815-82-5.

(8) Kishimato, K.; Ohta, M. *Nippon Kagaku Zasshi* **1962**, *83*, 833.

Direct Difluorovinylation of Tertiary Enolates

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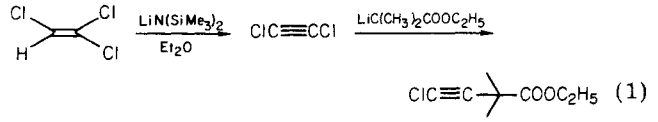
We have recently described a method for the efficient dichlorovinylation of tertiary ester and ketone enolates employing dichloroacetylene as a Michael acceptor.[1] In such reactions it has proven advantageous to generate preformed dichloroacetylene[2] and then react it with the enolate nucleophile (eq 1).



(1)

Since the literature suggests that difluoroacetylene is extremely unstable and probably not readily isolable,[3] we have attempted to achieve the difluorovinylation of eno-

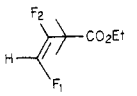
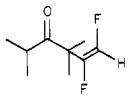
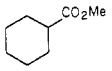
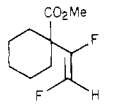
(1) (a) Kende, A. S.; Benechie, M.; Curran, D. P.; Fludzinski, P.; Swenson, W.; Clardy, J. *Tetrahedron Lett.* **1979**, 4513. (b) Kende, A. S.; Fludzinski, P. *Ibid.* **1982**, *23*, 2369. (c) Kende, A. S.; Fludzinski, P. *Ibid.* **1982**, *23*, 2373.

(2) Kende, A. S.; Fludzinski, P. *Synthesis* **1982**, 455.

(3) Syntheses have been limited to subjecting difluoromaleic anhydride to pyrolysis (600 °C) or to passing fluorocarbons through electrical discharge tubes; in both cases, difluoroacetylene was not isolated but only detected by mass spectrometry or gas chromatography. Bruce, M. I.; Cullen, W. R. In "Fluorine Chemistry Reviews"; Tarrant, P.; Ed., Marcel Dekker: New York, 1969; Vol. 4. The preparation and chemistry of fluoroacetylene and arylfluoroacetylenes have recently been reported: Sauvetre, R.; Normant, J. F. *Tetrahedron Lett.* **1982**, *23*, 4325. Martin, S.; Sauvetre, R.; Normant, J. F. *Ibid.* **1982**, *23*, 4329.

0022-3263/83/1948-1384$01.50/0

Table I. Difluorovinyl Adducts from Trifluoroethylene

entry	starting material	difluorovinyl adduct[a]	yield,[b] %
1			60
2			40
3			43

[a] All adducts gave ^{1}H NMR, MS, and IR consistent with proposed structures. [b] Yields based on amount of *tert*-butyllithium used.

lates by the in situ generation of this fluorinated Michael acceptor. We find that treatment of excess CF_2=CHF in THF with 1.0 equiv of *tert*-butyllithium at −78 °C, followed by addition of 4.0 equiv of a simple tertiary lithium enolate (from 4.0 equiv each of LDA, HMPA and carbonyl reactant in THF at 0 °C) at −78 °C and allowing the reaction to warm to room temperature, gave moderate yields (based on *t*-BuLi) of difluorovinyl adducts (Table I). Attempts to repeat the difluorovinylation without the presence of added *t*-BuLi led to only traces of the difluorovinyl adducts.

The regiochemistry and stereochemistry of the difluorovinyl adducts could be unequivocally assigned by the ^{1}H NMR. For example, the vinyl proton of the diflurovinyl adduct of ethyl isobutyrate appeared as a doublet of doublets at 6.91 ppm with J_{HF_1} = 76 Hz (geminal coupling)[4] and J_{HF_2} = 6 Hz (cis coupling).[4]

The requirement for *t*-BuLi to achieve appreciable product yields appears to implicate FC≡CF as an intermediate in these additions.[5] Although such evidence is circumstantial, a carbanion chain mechanism[6] analogous to that proven for our dichlorovinylations is consistent with these preliminary results.

Experimental Section

Proton nuclear magnetic resonance (NMR) spectra were recorded on a JEOL Model JNM-MH-100 spectrometer (100 MHz). Chemical shift data are reported in parts per million downfield from internal tetramethylsilane. Data are presented as follows: chemical shift (multiplicity, coupling constant, number of protons). The abbreviations used are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer and calibrated with the with the 1601 cm^{-1} peak of polystyrene. Low-resolution mass spectra were recorded on a Du Pont 21-490B mass spectrometer at 75 eV. M^+ signifies the molecular ion.

Tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA) were distilled from sodium–benzophenone. Diisopropylamine was distilled from calcium hydride. Reaction flasks were flame dried under a stream of nitrogen.

The silica gel used for medium-pressure chromatography (MPC) was EC/B Manufacturing Chemists, Inc., silica gel 60 (230–240 mesh). The solvent pump was supplied by Fluid Metering Inc., Oyster Bay, NY.

Chemical Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

General Procedure for Enolate Difluorovinylation. Diisopropylamine (400 mg, 4.0 mmol) was suspended in THF (5 mL) at 0 °C under nitrogen. A solution of 1.55 M *n*-butyllithium (2.6 mL, 4.0 mmol) was added and the solution stirred at 0 °C for 10 min. The ketone (4.0 mmol, neat) was added, followed immediately by the addition of HMPA (720 mg, 4.0 mmol). The enolate thus formed was stirred at 0 °C for 30 min.

In a separate flask, gaseous trifluoroethylene (excess) was condensed into a 50 mL flask at −78 °C under nitrogen. THF (10 mL) was added slowly, followed by 1.9 M *tert*-butyllithium (0.53 mL, 1.0 mmol). (The solution became pale yellow upon *tert*-butyllithium addition.) The solution was stirred at −78 °C for 20 min, followed by dropwise addition of the preformed enolate (prepared above). The solution was allowed to warm to room temperature over several hours, poured onto water, and extracted three times with diethyl ether. The combined extracts were washed four times with water, once with brine, and dried over magnesium sulfate. Purification by MPC (10% ethyl acetate in hexanes as the eluant) gave the products as colorless oils (homogeneous by NMR and TLC). Yields are based on the amount of *tert*-butyllithium used.

Ethyl (*E*)-3,4-Difluoro-2,2-dimethylbut-3-enoate (Table I, Entry 1). The above procedure was used by starting with ethyl isobutyrate: yield 60% homogeneous by NMR and TLC); NMR ($CDCl_3$) δ 6.91 (dd, *J* = 76, 6 Hz, 1 H), 4.10 (q, *J* = 7 Hz, 2 H), 1.44 (d, *J* = 1 Hz, 6 H), 1.24 (t, *J* = 7 Hz, 3 H); IR (CCl_4) 1780 (weak), 1740 (strong) cm^{-1}; MS, *m/e* 178 (M^+), 105 (100).

Kugelrohr distillation [bp 80–90 °C (15 torr)] gave an analytically pure sample. Anal. Calcd for $C_8H_{12}F_2O_2$: C, 53.92; H, 6.79; F, 21.33. Found: C, 53.95; H, 6.56; F, 21.10.

(*E*)-1,2-Difluoro-3,3,5-trimethylhex-1-en-4-one (Table I, Entry 2). The above procedure was used by starting with 2,4-dimethyl-3-pentanone: yield 40% (homogeneous by NMR and TLC); NMR ($CDCl_3$) δ 7.00 (dd, *J* = 76, 6 Hz, 1 H), 3.08 (m, 1 H), 1.38 (d, *J* = 1 Hz, 6 H), 1.06 (d, *J* = 7 Hz, 6 H); IR (neat) 1780 (sh), 1725 (s) cm^{-1}; MS, *m/e* 176 (M^+).

Methyl 1-[(*E*)-1,2-Difluorovinyl]cyclohexanecarboxylate (Table I, Entry 3). The above procedure was used by starting with methyl cyclohexanecarboxylate: yield 43% (homogeneous by NMR and TLC); NMR ($CDCl_3$) δ 7.02 (dd, *J* = 76, 6 Hz, 1 H), 3.70 (s, 3 H), 2.36–1.04 (m, 10 H); IR (neat) 1780 (sh), 1745 (s) cm^{-1}; MS, *m/e* 204 (M^+).

Registry No. Ethyl isobutyrate, 97-62-1; 2,4-dimethyl-3-pentanone, 565-80-0; methyl cyclohexanecarboxylate, 4630-82-4; trifluoroethylene, 359-11-5; ethyl (*E*)-3,4-difluoro-2,2-dimethylbut-3-enoate, 85066-79-1; (*E*)-1,2-difluoro-3,3,5-trimethylhex-1-en-4-one, 85066-80-4; methyl 1-[(*E*)-1,2-difluorovinyl]cyclohexanecarboxylate, 85066-81-5.

(4) Williams, H. D.; Fleming, I. "Spectroscopic Methods in Organic Chemistry", 2nd ed.; McGraw-Hill, New York, 1973; p 141.
(5) (a) Seyferth, D.; Welch, D. E.; Raab, G. *J. Am. Chem. Soc.* **1962**, *84*, 4266. (b) Viehe, H. G. *Angew. Chem., Int. Ed.* Engl. **1963**, *7*, 477.
(6) See ref 1b.