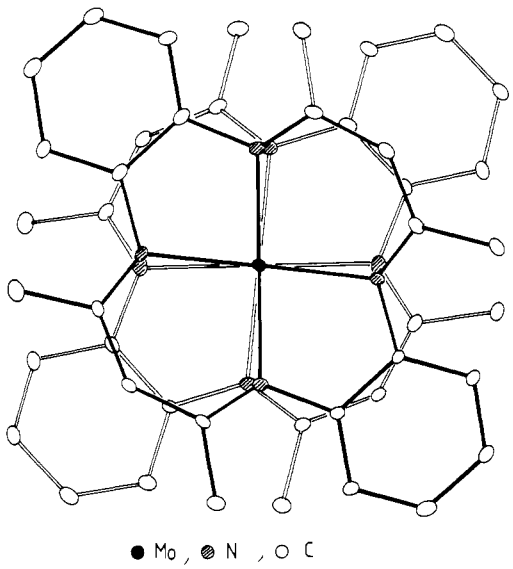


Figure 1. ORTEP plot of $[\{Mo(tmtaa)\}_2]^{++}$ viewed down the Mo–Mo bond axis illustrating the almost eclipsed configuration of the two MoN_4 moieties.

Treatment at low temperature of a THF solution of $tmtaaH_2$ with **2** equiv of *n*-BuLi affords, after warming up at 20 °C and crystallization (THF/n-hexane), pyrophoric bright red THF-solvated crystals of Li_2tmtaa (**2**) (see Scheme I). The diamagnetic compound **2** (ν(N=C=C=C=C=N) = 1545 cm^{-1}) is obtained in nearly quantitative yield.

At −30 °C, a THF solution of **2** reacts with 0.5 equiv of $Mo_2(OAc)_2$, affording, after extraction and crystallization (CH_2Cl_2/Et_2O), brown-black crystals of $[Mo(tmtaa)]_2$ (**3**) in 70% yield.

It is noteworthy that compound **3**, which is slightly air sensitive and unstable in solution, could not be obtained by reaction of $Mo_2(OAc)_4$ with $tmtaaH_2$ in various solvents, even in the presence of bases such as DBU.[13]

The cyclic voltammetry of **3** in acetonitrile (0.1 M Bu_4NPF_6; 200 mV/s) shows four redox processes corresponding to two reductions and two oxidations. The first reduction ($E^{1/2}$ = −0.90 V/Fc) and the firt oxidation ($E^{1/2}$ = −0.44 V/Fc) are associated with chemically and electrochemically reversible one-electron transfer steps. The second reduction wave ($E^{1/2}$ = −2.48 V/Fc) is irreversible (both chemically and electrochemically) whereas the second oxidation at $E^{1/2}$ = +0.42 V/Fc is an electrochemically reversible process. The magnitude of the second oxidation peak current suggests it is due to a two-electron transfer step. These results indicate that access to mixed-valence Mo^{II}/Mo^{III} and Mo^{I}/Mo^{II} complexes may be expected by chemical redox processes. Indeed the CV of **5** starting from 0 V/Fc is identical with that of **3** except that the redox process at −0.44 V/Fc is now a reduction wave.

Characterization of the unstable reduced species **4**, obtained by reduction of **3** with Na–Hg (toluene, −10 °C, 2 h), has been carried out by ESR spectroscopy. Evidence for the electron being delocalized over two molybdenum nuclei comes from the observation at room temperature of low-intensity 6- and 11-line spectra near the intense central signal (g = 1.964; A_{Mo} = 23.3 × 10^{-4} cm^{-1}).

Room-temperature oxidation of **3** with ferricinium salts is easily realized, quantitatively yielding the dark-purple cationic paramagnetic Mo^{II}/Mo^{III} species **5** as a thermally and air stable complex. ESR spectroscopy measurements (CH_2Cl_2; room temperature) are indicative of a $S = {}^1/_2$ metal-centered radical (g = 1.959; A_{Mo} = 32.2 × 10^{-4} cm^{-1}).

The X-ray crystal structure of **5** (Figure 1) confirms the dimeric nature of this species.[14] The two "saddle-shaped" ligands are rotated by nearly 90° relative to one another with the molybdenum atoms displaced 0.57 Å from the N_4 coordination mean plane. The eclipsed configuration of the two MN_4 moieties and the Mo–Mo distance of 2.221 (1) Å are consistent with a metal bond order of 3.5.[12] These parameters may be compared with those of the recently structurally characterized metalloporphyrin dimer, $[Mo(TPP))_2$, in which the Mo–Mo distance is 2.239 (1) Å, the Mo atoms are displaced 0.46 Å from the plane, and the two porphyrin moieties are rotated 18° relative to one another.[8]

In conclusion we would emphasize that use of the reactive species Li_2tmtaa instead of $tmtaaH_2$ constitutes an excellent approach for the synthesis of new tmtaa–metal derivatives. Further examples are presently under study.

Acknowledgment. Support of this research by D.R.E.T. (Direction des Recherches et Etudes Techniques) is gratefully acknowledged. We thank J. M. Kerbaol, F. le Floch, and Dr. P. Guenot for helpful experimental assitance.

Supplementary Material Available: Details for the X-ray structure determination of **5** including a listing of positional and thermal parameters and tables of bond lengths and angles, some analytical and spectroscopic (IR, ^1H NMR, ESR, MS) data for **2**, **3**, and **5** and ESR data for **4** (8 pages); table of structure factors for **5** (14 pages). Ordering of information is given on any current masthead page.

(13) Kerbaol, J. M., unpublished results. DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene.

(14) $[Mo(C_{22}H_{22}N_4)]_2PF_6$, CH_2Cl_2. Crystals are monoclinic, space group $C2/c$ with a = 34.483 (8) Å, b = 15.749 (5) Å, c = 16.991 (7) Å, β = 101.06 (6)°, V = 9056 (2) A^3, Z = 8, d_c = 1.625 g cm^{-3}, μ = 7.61 cm^{-1}. Intensity data were collected on a CAD-4 Enraf Nonius automated diffractomer with Mo Kα radiation up to a 2θ limit of 50°. The structure was solved by Patterson and Fourier methods and refined to present discrepancy indices R and R_w of 0.054 and 0.063, respectively, for 4599 independent reflections with $I > 4\sigma(I)$ out of 8836 unique data collected. The PF_6 anion and the CH_2Cl_2 solvate molecule are distributed on the same two general positions with a statistical occupancy of 0.5; then the PF_6 anion appears with a strongly distorted octahedral symmetry.

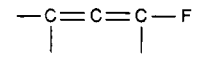
A Novel Route to Allenyl Fluorides. Synthesis of 4-Amino-7-fluorohepta-5,6-dienoic Acid, the First Fluoroallenyl Amino Acid[1]

Arlindo L. Castelhano and Allen Krantz*

Syntex Inc., Mississauga, Ontario, Canada L5N 3X4

Received March 5, 1987

Although both fluorine and allene chemistry are active areas of research, there are few documented examples of fluoroallenes,[2,3]



This type of functional group is not only of fundamental chemical interest but could also have important applications in the design of enzyme-activated irreversible inhibitors[4] and other biologically active species. It is well-known, for example, that the replacement of a hydrogen by a fluorine atom at saturated and unsaturated carbon centers of enzyme substrates[5,6] and inhibitors[7] can have profound metabolic consequences.

However, the lack of a practical route to fluoroallenes has limited their availability. We wish to report a simple and efficient means of preparing fluoroallenes that avoids the use of highly

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(2) Dolbier, W. R., Jr.; Burkholder, C. R.; Piedrahita, C. A. *J. Fluorine Chem.* **1982**, *20*, 637.
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0002-7863/87/1509-3491$01.50/0

reactive and corrosive materials and allows the introduction of a fluoroallenyl moiety into compounds containing a variety of functional groups (eq 1). The synthesis features a fluoro-

$$\underset{\mathbf{3}}{RC{\equiv}CLi} + \underset{\mathbf{2}}{CHFCl_2} \xrightarrow[-100\text{ to }-70\ ^\circ C]{THF} \underset{\mathbf{1}}{RC{\equiv}CCHFCl} \xrightarrow{AlH_3} \underset{\mathbf{4}}{RCH{=}C{=}CHF} \quad (1)$$

R (yield for **1**) = (**a**) n-C_5H_{11} (30%); (**b**) TMS (40–50%); (**c**) $THPOCH_2$ (50–70%); (**d**) $THPOCH(CH_3)$ (70%); (**e**) Ph (57%); (**f**) $TBSO(CH_2)_3CH(OTHP)$ (50–60%)

chloropropargyl synthon, which is produced by the reaction of $CHFCl_2$ with the requisite acetylide[8] and is convertible to fluoroallene upon reduction with aluminum hydride.

For acetylides **3a–f**, the propargyl dihalide **1** is conveniently prepared in good yield by adding freon **2** (1.5–2.0 equiv) to the lithium acetylide[9] **3a–f** at −100 °C in THF. When the dark reaction mixture reaches −70 °C, it is neutralized with 1.0 M citric acid and product **1** is then extracted with ether.[10]

Reductive displacement of chloride by treating **1** in THF with 5 equiv of AlH_3 at room temperature for 3–5 days gives **4** in ca. 70% yield. Reductive alkylation of **1** can also be accomplished by using Crabbe's organocuprate methodology.[11,12] Substrates containing hydroxyl or an amido nitrogen linked to the propargylic position distal to the halides are rapidly reduced with AlH_3 at 0 °C in 1 h (for such substrates overreduction to terminal acetylenes occurs if the reaction is carried out at room temperature). The fluoroallenes **4** are easily discerned by their typical spectral parameters[2,3] as in the case of the diastereomers **4c**: ν_{max} = 1977 cm^{-1} (C=C=C); ^1H NMR (80 MHz, $CDCl_3$) δ 6.03, 6.06 (dt, 1 H, J = 1.5, 5.5 Hz, HC=C=C), 7.13 (ddm, 1 H, J = 5.4, 85.6 Hz, C=C=CHF); ^{19}F NMR[16b] (75 MHz, $CDCl_3$) δ −164.5, −164.62 (two ddt, J = 1.7, 8.8, 86.1 Hz).

The availability of **1b** permits the direct introduction of the moiety −C≡CCHFCl into organic molecules.[13] Thus desilylating **1b** with $(n\text{-}Bu)_4N^+F^-$/−70 °C/THF in the presence of an aldehyde or ketone generates alcohol **6**, which can then be reduced as above (0 °C) to the fluoroallene-alcohol **7** (eq 2).

$$\underset{\mathbf{1b}}{TMS{-}C{\equiv}CCHFCl} + \underset{\mathbf{5}}{RC(=O)R'} \xrightarrow[-70\ ^\circ C]{F^-/THF} \underset{\mathbf{6}}{RC(OH)(R')C{\equiv}CCHFCl} \xrightarrow{AlH_3} \underset{\mathbf{7}}{RC(OH)(R')CH{=}C{=}CHF} \quad (2)$$

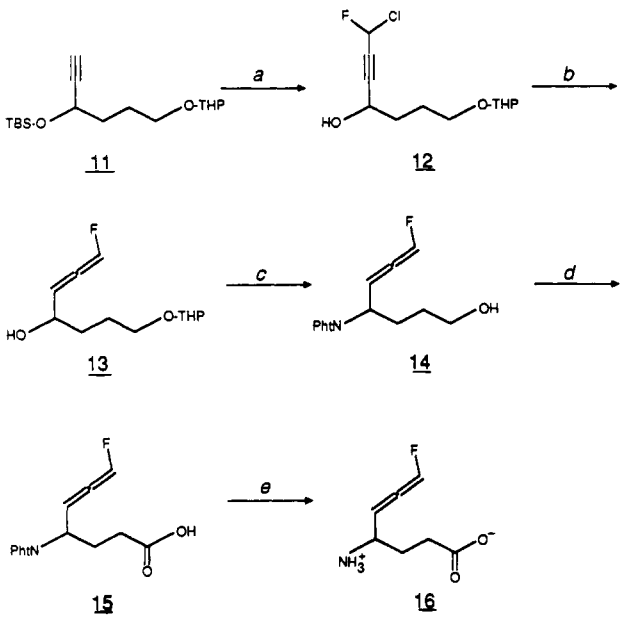
Recently, allenylamines[14] and allenyl amino acids[15] have been prepared and shown to be suicide inhibitors of mitochondrial monoamine oxidase (EC 1.4.3.4, MAO) and specific vitamin B-6 dependent enzymes, respectively. Alcohol **8**, obtained by aqueous hydrolysis of **1c**, is a useful precursor of the corresponding fluorine-substituted allenylamines **9** and **10** (eq 3).[16a] In addition,

$$\underset{\mathbf{9}}{HFC{=}C{=}CHCH_2NH_2} \xleftarrow{a} \underset{\mathbf{8}}{HOCH_2C{\equiv}CCHFCl} \xrightarrow{b} \underset{\mathbf{10}}{HFC{=}C{=}CHCH_2N(CH_3)CH_2Ph} \quad (3)$$

(a) (1) succinimide/DEAD/Ph_3P;[22] (2) $NaBH_4$; (3) DHP/PPTS;[18] (4) AlH_3; (5) $(Boc)_2O$/DMAP; LiOH;[25] (6) TsOH, (b) (1) MsCl/NEt_3; (2) $PhCH_2NHCH_3$; (3) AlH_3 room temperature

we have applied the homologation–reduction sequence (Scheme I) to the synthesis of 4-amino-7-fluorohepta-5,6-dienoic acid (**16**), a potential suicide inhibitor of GABA transaminases. Reaction of the bis-protected diol **11**[17] with $CHFCl_2$ as in eq 1, followed by $(n\text{-}Bu)_4N^+F^-$ treatment, generated **12** (50% overall yield), which was then reduced with AlH_3 at 0 °C to provide **13** (70% yield). The Mitsunobu[22] reaction of **13** with phthalimide followed by MeOH/PPTS[18] furnished the phthalamido alcohol **14** (40–50% yield). Jones oxidation[23] of **14** gave the corresponding phthalimido

Scheme I[a]



[a] (a) (1) n-BuLi/−70 °C; (2) $CHFCl_2$/−100 °C; (3) n-$Bu)_4N^+F^-$/THF (50%). (b) AlH_3/0 °C/1 h (70%). (c) (1) phthalimide/DEAD/Ph_3P; (2) MeOH/PPTS (40–45%). (d) CrO_3/H^+ (≈70%). (e) (1) $NaBH_4$/EtOH; (2) HOAc/Δ (≈55%).

(8) Acetylide **3** was prepared at −70 °C by the dropwise addition of 1.05 equiv of 1.5 M n-BuLi to the corresponding acetylene in dry THF for 15 min.

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(10) The product, which usually contains 20–25% of unreacted starting material, is purified by distillation or flash chromatography. The fluorochloropropargyl moiety of **1** is apparent in IR and NMR spectra. For example, **1c** has ν_{max} = 2250 cm^{-1} (m) (C≡C); ^1H NMR (80 MHz, $CDCl_3$) δ 6.6 (dt, 1 H, J = 1.2, 50.5 Hz, C*H*FCl, ^{19}F NMR[16b] (75 MHz, $CDCl_3$) δ −129.54 (dt, J = 5.6, 50.6 Hz).

(11) Baret, P.; Barreiro, E.; Greene, A. E.; Luche, J.-L.; Teixeira, M.-A.; Crabbe, P. *Tetrahedron* **1979**, *35*, 2931.

(12) For example, treatment of **1c** with lithium dimethyl cuprate–dimethyl sulfide gave 4-OTHP-1-fluoro-3-methylbuta-1,2-diene (48%): IR ν_{max} 1980 cm^{-1} (m) (C=C=C); ^1H NMR ($CDCl_3$) δ 7.0 (dm, J = 89.6 Hz, HFC=C=C); ^{19}F NMR[16b] ($CDCl_3$) δ −160.33, −160.42.

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(16) (a) **9**·TsOH: mp 118–120 °C dec; IR (KBr) ν_{max} 1990 cm^{-1} (C=C=C); ^1H NMR (80 MHz, Me_2SO-d_6) δ 2.3 (s, 3 H, CH_3), 3.65 (br m, 2 H, CH_2N), 6.25 (dq, 1 H, J = 2.4, 4.8 Hz, CH=C=C), 7.1, 7.45 (2 d, 4 H, Ph), 7.6 (dm, 1 H, J = 84.4 Hz, HFC=C=C), 8.0 (br m, 3 H, NH_2, TsOH); ^{19}F NMR[16c] (75 MHz, Me_2SO-d_6) δ −160.99; MS (EI), m/z 87 (M^+). Anal. Calcd for $C_{11}H_{14}FNO_3S$: C, 50.95; H, 5.44; N, 5.4. Found: C, 50.70; H, 5.47; N, 5.2. **10**-oxalate: mp 118–120 °C dec; IR (free amine ν_{max} 1973 cm^{-1} (C=C=C); ^1H NMR (300 MHz, D_2O δ 2.9 (s, 3 H, N-CH_3), 3.95 (br s, 2 H, NCH_2CH=), 4.45 (br d, 2 H, NCH_2Ph), 6.25 (br q, 1 H, J = 6.7 Hz, HC=C=C), 7.58 (dd, 1 H, J = 5.33, 83.4 Hz, HFC=C=C), 7.55 (m, 5 H, Ph); ^{19}F NMR[16c] (75 MHz, D_2O) δ −165.12 (br d, J = 83.0 Hz); MS (EI), m/z 191 (M^+). Anal. Calcd for $C_{14}H_{16}FNO_4$: C, 59.78; H, 5.73; N, 4.98. Found: C, 59.59; H, 5.72; N, 4.93. (b) $CFCl_3$ used as the internal standard. (c) External TFA used as reference, assigned as −78.9 ppm.

(17) Compound **11** was prepared from 3-buten-1-ol. THP protection of this alcohol[18] followed by hydroboration[19] and modified Moffatt oxidation[20] gave 4-OTHP-butanal in >90% overall yield. Condensation of this aldehyde with TMSC≡CLi, followed by $(n\text{-}Bu)_4N^+F^-$ treatment and protection with TBSCl,[21] gave **11** in >95% yield.

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acid **15**, from which the amino acid **16** was derived under Ganem's conditions.[24] Following ion-exchange chromatography (Bio-Rad Ag 50W-X8, eluting with 20% aqueous pyridine) and crystallization from acetone–water, **16** was obtained as white fluffy crystals: mp 118–120 °C dec; IR (KBr) ν_{max} 1990 cm^{-1} (C=C=C); ^1H NMR (80 MHz, D_2O) δ 1.9–2.7 (m, 4 H, CH_2CH_2), 4.05 (m, 1 H, CHN), 6.25 (br t, 1 H, $J \approx 5.4$ Hz, HC=C=C), 7.5 (ddd, 1 H, J = 1.5, 5.6, 84.5 Hz, HFC=C=C); ^{19}F NMR[16c] (75 MHz, D_2O) δ −160.9 (br dd, J = 8.44, 84.6 Hz). Anal. Calcd for $C_7H_{12}FNO_3$: C, 47.45; H, 6.83; N, 7.91. Found: C, 47.92; H, 6.08; N, 7.85. MS, m/z (EI) 139 $(M - HF)^+$, (CI, NH_3) 160 (MH^+).

In summary, a simple and versatile two-step synthesis of fluoroallenes from acetylenes has been described. Use of this methodology resulted in the preparation of the multifunctional amines **9** and **10** and amino acid **16**. Fluoroallene chemistry and enzymology is currently under investigation.

Acknowledgment. We are grateful to Valerie Robinson for her valuable assistance with NMR spectroscopy.

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A New Tri-*n*-butyltin Hydride Based Rearrangement of Bromomethyl β-Keto Esters. A Synthetically Useful Ring Expansion to γ-Keto Esters

Paul Dowd* and Soo-Chang Choi

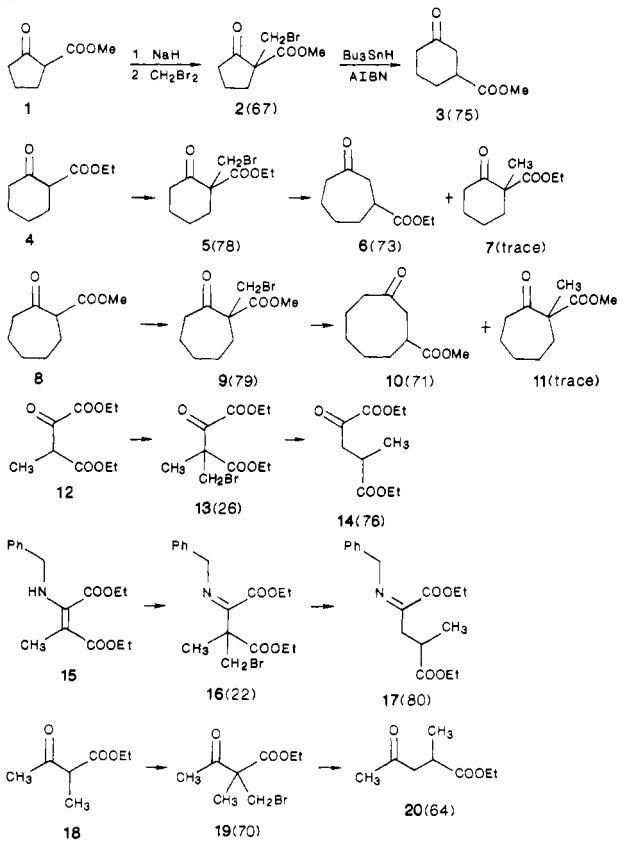
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260
Received February 4, 1987

The universal presence of five- and six-membered ring ketones among organic molecules has made the Dieckmann condensation[1] a central ring-forming reaction in organic chemistry. The utility of the Dieckmann condensation is further enhanced by the alkylation–decarboxylation sequence leading to a virtually limitless variety of α-substituted cyclopentanones and cyclohexanones. Any additional flexibility that serves to enlarge the scope of the Dieckmann condensation will be valuable, since this reaction is an important component of synthetic design.[1] We have discovered a novel adjunct to the Dieckmann reaction that permits convenient and completely regioselective ring expansion of the β-keto ester Dieckmann products. It is of special value because it permits the easy preparation of seven- and eight-membered rings.

In a representative sequence, reaction of methyl 2-cyclopentanonecarboxylate (**1**) with dibromomethane and sodium hydride in refluxing tetrahydrofuran yielded the bromomethyl adduct **2**. When the latter was treated with tri-*n*-butyltin hydride in refluxing benzene with a catalytic amount of AIBN, smooth rearrangement to the ring-expansion product, methyl 3-cyclohexanonecarboxylate (**3**), occurred in 75% yield. Likewise (Table I), the six- and seven-membered ring β-keto esters **4** and **8** undergo regiospecific ring expansion by a one-carbon unit to the seven- and eight-membered γ-keto esters **6** and **10**. The open-chain β-keto esters **12** and **18** and even the corresponding enamine **15** undergo chain extension to **14**, **20**, and **17** in good yield by this method (Table I).[2-4]

Much remains to be done to establish the mechanism of these reactions with finality, but it seems reasonable at this stage to assume that the ring-expansion reaction involves the generation of free radical intermediates and that attack on the carbonyl group is the key step in the rearrangement. The literature contains strong indications that this should be a viable process.[5-8] Thus, we envision (Scheme I)[9] that the reaction proceeds through tri-*n*-butyltin hydride promoted production of the primary radical followed by attack of the latter on the neighboring carbonyl group.[11] The resulting alkoxy radical then undergoes ring cleavage to yield the stabilized radical adjacent to the ester.

Table I. Tri-*n*-butyltin Hydride Promoted Rearrangement of Bromomethyl Substituted β-Keto Esters (% Isolated Yield)[a]



[a] All new substances had satisfactory NMR, IR, and mass spectra, including exact mass determination. [b] The NMR spectrum, the mass spectrum and the exact mass determination established the identity of the product Schiff base **17**, but chromatographic isolation yielded the keto ester **14**.

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