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); ^{1}H 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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(23) Baumgarten, H. E. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 866.

(24) Osby, J. O.; Martin, M. G.; Ganem, B. *Tetrahedron Lett.* **1984**, 2093.

(25) Flynn, D. L.; Zelle, R. E.; Grieco, P. A. *J. Org. Chem.* **1983**, *48*, 2424.

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

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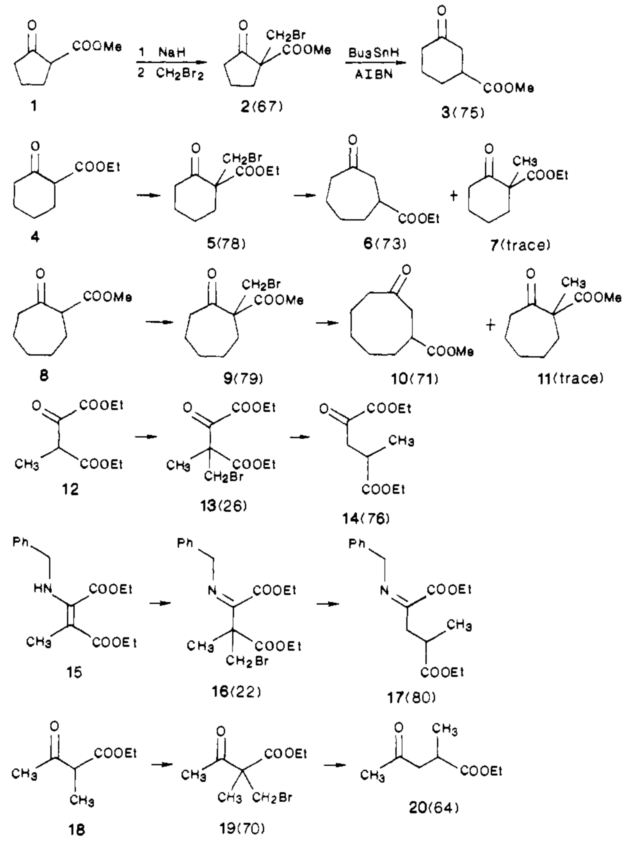
The universal presence of five- and six-membered ring ketones among organic molecules has made the Dieckmann condensation[1] a central ring-forming reaction in organic chemistry. The utility of the Dieckmann condensation is further enhanced by the alkylation–decarboxylation sequence leading to a virtually 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]

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**.

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.

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(1) Schaeffer, J. P.; Bloomfield, J. J. *Org. React.* **1967**, *15*, 1.

(2) An enzymic β- to γ-keto acid rearrangement has been described by: Michenfelder, M.; Retey, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 366.

(3) Tri-*n*-butyltin hydride promoted migration of a thioester has been reported by: Wollowitz, S.; Halpern, J. *J. Am. Chem. Soc.* **1984**, *106*, 8319. Tada, M.; Inoue, K.; Sugawara, K. *Chem. Lett.* **1985**, 1821. Tada, M.; Inoue, K.; Okabe, M. *Ibid.* **1986**, 703.

(4) For ring expansion of a cobaloxime complex of 2-methylene-2-cyclopentanonecarboxylate, see: Okabe, M.; Osawa, T.; Tada, M. *Tetrahedron Lett.* **1981**, *22*, 1899. Lowe, J. N.; Ingraham, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 3801.

(5) Bentrude, W. G.; Danall, K. R. *J. Am. Chem. Soc.* **1968**, *90*, 3588.

(6) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 8102. Nickon, A.; Iwadare, T.; Maguire, F. J.; Mahajan, J. R.; Narang, S. A.; Umezawa, B. *J. Am. Chem. Soc.* **1970**, *92*, 1688. Spero, G. B.; Thompson, J. L.; Schneider, W. P.; Kagan, F. *J. Org. Chem.* **1963**, *28*, 755. Suginome, H.; Sato, N.; Masumune, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 215. Suginome, H ; Sato, N.; Masumune, T. *Tetrahedron Lett.* **1967**, 1557. Heusler, K.; Kalvoda, J. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 525.

(7) Giese, B.; Horler, H. *Tetrahedron Lett.* **1983**, *24*, 3221. Giese, B.; Horler, H. *Tetrahedron* **1985**, *41*, 4025. Giese, B.; Heinrich, N.; Horler, H.; Doch, W.; Schwartz, H. *Chem. Ber.* **1986**, *119*, 3528.

(8) For other free radical based ring expansion reactions see: (a) Riemann, H.; Capomaggi, A. S.; Strauss, T.; Oliveto, E. P.; Barton, D. H. R. *J. Am. Chem. Soc.* **1961**, *83*, 4481. (b) Reusch, W.; Johnson, C. K.; Manner, J. A. *J. Am. Chem. Soc.* **1966**, *88*, 2803. We thank Professor Lawrence Montgomery for ref 8b.

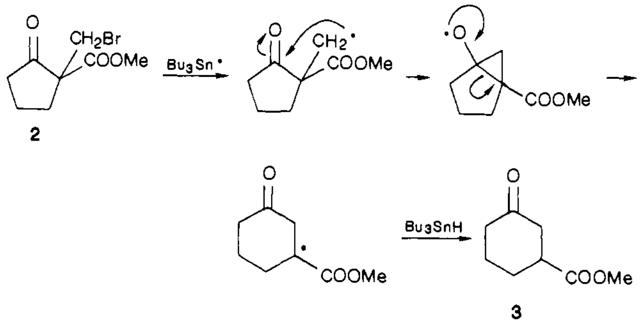
(9) This is simply a preference. We cannot, at this stage, rule out a fragmentation to the acyl radical[8a] followed by recombination and attack on the acrylate, or an electron-transfer mechanism.[10] Future experiments will address these problems.

(10) Tanner, D. D.; Haribansh, K. S. *J. Org. Chem.* **1986**, *51*, 5182.

(11) For leading references to recent work on the formation on carbon–carbon bonds using free radical intermediates, see: Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. Hart, D. J.; Tsai, Y.-M. *J. Am. Chem. Soc.* **1982**, *104*, 1430. Curran, D. P.; Rakiewicz, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 1448. Koreeda, M.; George, I. A. *J. Am. Chem. Soc.* **1986**, *108*, 8098.

0002-7863/87/1509-3493$01.50/0

Scheme I



In addition to the insertion product, we also observe the direct reduction products **7** and **11** in the seven- and eight-membered ring-forming reactions. This undesired branch in the reaction can be completely suppressed by carrying out the reaction under dilute conditions in which the tri-*n*-butyltin hydride is added slowly with a syringe drive. Direct reduction is not a problem with the five-membered ring (Table I, entry a) which undergoes ring expansion under normal conditions of concentration (5 mM). In this instance, ring closure is fast relative to the chain transfer that leads to unrearranged reduction product.

There is an interesting sidelight. As noted above, we find that the Schiff base **16** rearranges readily under these circumstances. The latter does not rearrange (in a parallel investigation[12]) upon treatment with vitamin B_{12s}, whereas the α-keto ester **13** rearranges when treated with either tri-*n*-butyltin hydride or with vitamin B_{12s}.

The transformation reported here constitutes an alternative to the Nagata reaction and may be useful in instances where the appropriate α,β-unsaturated ketone is not readily available.

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(12) Dowd, P.; Choi, S.-C., unpublished results.

Observation of Plasmon Frequency in the Optical Spectrum of $Au_{18}Ag_{20}$ Cluster: The Beginning of the Collective Phenomenon Characteristic of the Bulk?

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Recently there has been considerable interest in the fundamental question of when, where, and how the metallic character begins and ends.[2-7] In other words, how many metal atoms must one put together in a cluster before it begins to look and behave like a metal? Conversely, how fine a metal particle must be before it ceases to be a metal? As cluster size increases from $\sim 10^2$ atoms to $\sim 10^3$ atoms, there is a transition from one extreme of chemical and physical behavior of molecular species to the other extreme of bulk properties. It is generally believed, and in many cases has been demonstrated, that unusual size-dependent properties can occur in the intermediate size range, the quantum size regime,[2-7] where there are tens to thousands of atoms. The fact that discrete metal clusters[8] of definitive size and shape provide an opportunity to study the evolution of band structure from the atomic to the solid state has sparked intense interest in the synthesis and characterization of high-nuclearity metal-cluster systems.

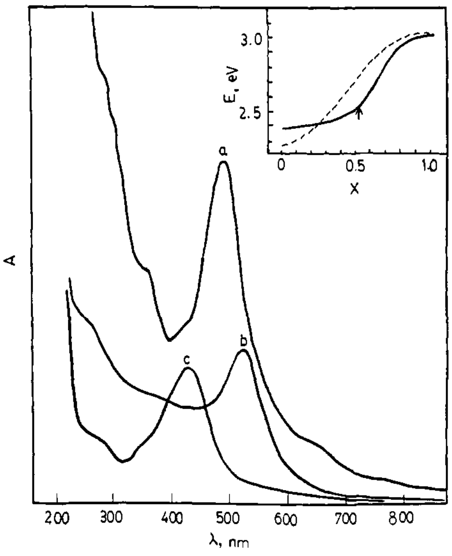

Figure 1. Optical (UV-vis) spectra of (a) $(Ph_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ (**1**) in ethanol, (b) colloidal Au particles in aqueous solution, and (c) colloidal $Au_{0.22}Ag_{0.78}$ particles in aqueous solution. Inset: solid curve, composition dependence of the energy of plasmon frequency of colloidal Au-Ag particles in aqueous solution; dashed curve, computer simulation. The arrow indicates the position for the $Au_{18}Ag_{20}$ (**1**) cluster.

Recently we reported the synthesis and structure of a novel 38-atom cluster $(Ph_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ (**1**).[9] The metal framework can be described as a *three*-centered icosahedra sharing three vertices in a cyclic (triangular) manner plus two capping atoms on the 3-fold axes (nuclearity = 3 × 13 − 3 + 2 = 38), measuring approximately 15 Å in diameter. Its optical spectrum is depicted in Figure 1, curve a. The most striking feature is the 495-nm absorption maximum in the visible region responsible for the intense cherry-red color of the solution.[10] This absorpton fre-

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(1) (a) AT&T Bell Laboratires. (b) University of Illinois, Chicago. (c) State University of New York.

(2) Teo, B. K.; DiSalvo, F. J.; Waszczak, J. V.; Longoni, G.; Ceriotti, A., *Inorg. Chem.* **1986**, *25*, 2262.

(3) (a) Benfield, R. E.; Edwards, P. P.; Stacy, A. M. *J. Chem. Soc., Chem. Commun.* **1982**, 525. (b) Johnson, D. C.; Benfield, R. E.; Edwards, P. P.; Nelson, W. J. H.; Vargas, M. D. *Nature (London)* **1985**, *314*, 231.

(4) (a) Ozin, G. A.; Mitchell, S. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 674. (b) Dietz, T. G.; Duncan, M. A.; Powers, D. E.; Smalley, R. E. *J. Chem. Phys.* **1981**, *74*, 6511. (c) Rohlfing, E. A.; Cox, D. M.; Kaldor, A., *Chem. Phys. Lett.* **1983**, *99*, 161.

(5) (a) Monot, R.; Narbel, C.; Borel, J.-P. *Nuovo Cimento B* **1974**, *19*, 253. (b) Borel, J.-P.; Millet, J.-L. *J. Physique* **1977**, *C2*, 115. (c) Knight, W. D. *Ibid.* **1977**, *C2*, 109. (d) Rossetti, R.; Nakahara, S.; Brus, L. E. *J. Chem. Phys.* **1983**, *79*, 1086. (e) Yee, P.; Knight, W. D. *Phys. Rev. B* **1975**, *11*, 3261. (f) Kappes, M. M.; Schar, M.; Radi, R.; Schumacher, E. *J. Chem. Phys.* **1986**, *84*, 1063.

(6) (a) Kubo, R. *J. Phys. Soc. Jpn.* **1962**, *17*, 975. (b) Kawabata, A.; Kubo, R. *J. Phys. Soc. Jpn.* **1966**, *21*, 1765.

(7) (a) Messmer, R. P.; Knudson, S. K.; Johnson, K. H.; Diamond, J. B.; Yang, C. Y. *Phys. Rev. B* **1976**, *13*, 1396. Yang, C. Y.; Johnson, K. H.; Salahub, D. R.; Kaspar, J.; Messmer, R. P. *Ibid.* **1981**, *24*, 5673. (b) Baetzoid, R. C.; Mason, M. G.; Hamilton, J. F. *J. Chem. Phys.* **1980**, *72*, 366. (c) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305; **1979**, *101*, 2604. (d) Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1980**, *197*, 233. (e) Teo, B. K. *J. Chem. Soc., Chem. Commun.* **1983**, 1362.

(8) For reviews on transition-metal clusters, see, e.g.: (a) Chini, P. *Gazz. Chim. Ital.* **1979**, *109*, 225. (b) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37. (c) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285; (d) *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley-Interscience: Chichester, 1980. (e) Teo, B. K. *Inorg. Chem.* **1985**, *24*, 1627. (f) Teo, B. K. *Inorg. Chem.* **1985**, *24*, 4209.

(9) Teo, B. K.; Hong, M. C.; Zhang, H.; Huang, D. B., submitted for publication. See also: *Chem. Eng. News* **1987**, *65*, 21.

(10) To date, attempts to observe the fine structure of the 495-nm peak at low temperatures were unsuccessful.