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Supplementary Material Available: Detailed information on the physical properties of all new compounds and X-ray crystal analysis of **4b** (15 pages); listing of observed and calculated structure factors for **4b** (5 pages). Ordering information is given on any current masthead page.

Free-Radical Cyclizations Promoted by Allylic *O*-Stannyl Ketyls: The Intramolecular Coupling of the β -Carbons of Activated Alkenes

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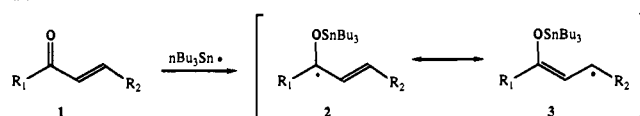
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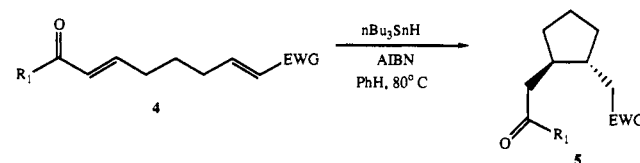
Free-radical-cyclization reactions have gained distinction in total synthesis and in new synthetic methodology and have been the focus of many recent important studies.¹ Much of this chemistry utilizes well-established precursors to carbon-centered radicals, such as halides, alkenes, alkynes, selenides, and sulfides, which are usually tethered to a suitable free-radical acceptor to produce cyclic derivatives when treated with tributyltin hydride. An α,β -unsaturated ketone or aldehyde is not generally considered to be a good precursor to a carbon-centered radical in these cyclizations; however, an allylic *O*-stannyl ketyl moiety^{2,3} should be produced by the reaction of the enone functional group with a trialkyltin radical.³ The *O*-stannyl ketyl radical would be resonance stabilized by the adjacent olefin moiety, which would provide interesting synthetic avenues to explore. It is also noteworthy that the stannyl enolate produced in this reaction can provide yet a second type of reactivity with these intermediates. If one can isolate the radical character from the nucleophilic character of the allylic *O*-stannyl ketyl by sequential reactions, an untapped reservoir of one- and two-electron reactions should result. This is important because the sequencing of one- and two-electron reactions is rapidly emerging as an important synthetic tool.⁴ These observations are in direct contrast to how an α,β -unsaturated ketone is normally viewed in free-radical and nucleophilic reactions, where it often functions as an electron acceptor in 1,4-addition reactions at the β -carbon of the olefin with many one- and two-electron donors. Although the *O*-stannyl ketyl resonance contributors **2** and **3**, shown in Scheme I, should provide useful manifolds of concurrent two-electron reactions and one-electron cyclizations, they have not been used in this capacity prior to the studies outlined herein.

We now report in preliminary results that free-radical cyclizations with unsaturated ketone precursors, shown in Scheme II, afford substituted cyclopentane rings and bicyclo[3.3.0] ring systems. To our knowledge, the method outlined herein is a new *reagent-based* approach to the β -coupling⁵ and cyclization of two

Scheme I



Scheme II^a



^aEWG = COCH₃, CN, CO₂CH₃.

Scheme III

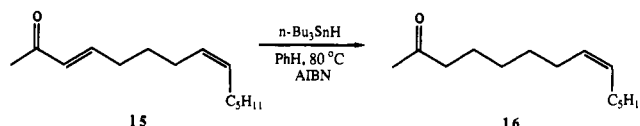


Table I. Cyclizations at the β -Carbons of Activated Alkenes

Starting Diene ^a	Products ^b
	+ 2.1 : 1 85%
	+ 3.0 : 1 94%
	+ 3.5 : 1 93%

^aStarting dienes were prepared by standard methods.¹⁰ ^bA general procedure is shown in footnote 11.

activated alkenes and it complements the only other currently available technique, electrochemical hydrodimerization.⁶ The studies also show that a bifurcation in the reactivity pathways of the radical and anion of the *O*-stannyl ketyl can be achieved and these intermediates can be induced to react independently in the same molecule, providing examples of sequential one- and two-

(1) (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: New York, 1986. (b) Neumann, W. P. *Synthesis* 1987, 665. (c) Ramaiah, M. *Tetrahedron* 1987, 43, 3541. (d) Curran, D. P. *Synthesis* 1988, 417, 489. (e) Hart, D. J. *Science* 1984, 223, 883.

(2) (a) Sugawara, T.; Otter, B. A.; Ueda, T. *Tetrahedron Lett.* 1988, 75. (b) Beckwith, A. L. J.; Roberts, D. H. *J. Am. Chem. Soc.* 1986, 108, 5983. (c) Enholm, E. J.; Prasad, G. *Tetrahedron Lett.* 1989, 4939.

(3) For a review of the preparation of *O*-stannyl ketyls by the reduction of carbonyls with trialkyltin radicals, see: Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: Boston, 1987.

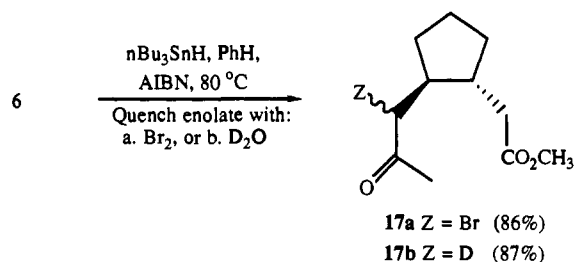
(4) (a) Kagan, H. B.; Namy, J. L.; Girard, P. *Tetrahedron* 1981, 37(Suppl. 1), 175. (b) Takai, K.; Nitta, K.; Fujimura, O.; Utimoto, K. *J. Org. Chem.* 1989, 54, 4732. (c) Curran, D. P.; Fevig, T. L.; Totleben, M. J. *Synlett* 1990, 733. (d) Molander, G. A.; Harring, L. S. *J. Org. Chem.* 1990, 55, 6171. (e) Molander, G. A.; Kenny, C. J. *Org. Chem.* 1991, 56, 1439.

(5) There are only a few examples of a sodium-promoted *intermolecular* coupling of the β -carbons of activated alkenes. Most cases involve enones blocked on both ends (usually with *tert*-butyl groups): (a) Bowers, K. W.; Giese, R. W.; Grimshaw, J.; House, H. O.; Kolodny, N. H.; Kronberger, K.; Roe, D. K. *J. Am. Chem. Soc.* 1970, 92, 2783. (b) House, H. O.; Giese, R. W.; Kronberger, K.; Kaplan, J. P.; Simeone, J. F. *J. Am. Chem. Soc.* 1970, 92, 2800.

(6) For two excellent recent reviews on (non-reagent-based) electrochemical methods of β -coupling of activated olefins, see: (a) Fry, A. J. *Synthetic Organic Electrochemistry*; J. Wiley & Sons, New York, 1989; Chapter 7. (b) Little, R. D.; Baizer, M. M. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 14.

Table II. Dilution Experiments with Methyl (2*E*,7*E*)-9-Oxo-2,7-decadienoate (**6**)

6 $\xrightarrow{n\text{-Bu}_3\text{SnH (1.1 equiv)}}$ 7 + 8		
	reaction conditions	7:8 (% yield)
1.	1.00 M 6 in benzene	9:1 (75)
2.	0.10 M 6 in benzene	25:1 (82)
3.	0.01 M 6 in benzene	>50:1 (82)

Scheme IV

electron cyclizations promoted by tributyltin hydride. In addition, excellent anti stereoselectivities (>50:1) with the ring appendages are achievable in this reversible 5-*exo-trig* free-radical cyclization.

We have initially examined three substrates, shown in Table I, which successfully underwent free-radical cyclization to produce a cyclopentane ring with anti-disposed appendages as the major product in each case. Variation of the electron-withdrawing group in each example did not appear to alter the ratios to any significant extent. The major and minor products were both formed by an initial one-electron cyclization to give the cyclopentane ring. The minor product, produced from syn-disposed appendages, underwent a second cyclization to render bicyclo[3.3.0] ring systems, not possible with the major anti isomers because of ring strain. These tandem ring cyclizations likely arise from the *O*-stannyl enolate reacting in a two-electron aldol-type condensation to afford the second ring. It is also interesting to note that in one minor product, compound **14**, four stereogenic centers were created; however, only the single diastereomer shown was observed. The stereochemistry was confirmed by difference NOE studies.⁷

The activated alkene acceptor appears to be a prerequisite for success in these reactions. When we attempted the cyclization with **15**,⁸ shown in Scheme III, only reduction of the olefin portion of the enone was observed.⁹ It would appear that intermolecular hydrogen atom transfer from tributyltin hydride is more rapid to radical species **3** when compared to the slower rate of cyclization with an unactivated alkene.

When the cyclization of **6** was examined at greater dilution, we were delighted to obtain much higher levels of stereoselectivity; note Table II. A ratio of >50:1 for the anti:syn products could be achieved at 0.01 M in benzene. The increase in stereoselectivity

(7) A summary of the difference NOE experiments is provided in the "Supplementary Material" section.

(8) **15** was prepared from 2-hydroxytetrahydropyran by treatment with (a) $\text{Ph}_3\text{P}=\text{CHC}_6\text{H}_{11}$, THF, 0 °C; (b) PDC, CH_2Cl_2 , HOAc (cat.), 4-Å sieves; (c) $\text{Ph}_3\text{P}=\text{CHCOCH}_3$, CH_2Cl_2 .

(9) We have also examined the cyclization of these substrates with SmI_2 , which should produce the allylic *O*-samarium ketyl analogues of **2** and **3**. Unfortunately, treatment of **6** with 2 equiv of SmI_2 in THF-methanol at -78 °C led to a low yield of an acyclic product by simple reduction of the enone alkene (as in **16**) along with several unidentified minor products.

(10) The diene starting materials were prepared in good yields in two ways. In the first method, freshly distilled glutaric dialdehyde was treated sequentially with (a) $\text{Ph}_3\text{P}=\text{CHCOCH}_3$, CH_2Cl_2 ; (b) $\text{Ph}_3\text{P}=\text{CH-EWG}$, CH_2Cl_2 . In the second method, 2-hydroxytetrahydropyran was treated sequentially with (a) $\text{Ph}_3\text{P}=\text{CHCOCH}_3$, CH_2Cl_2 ; (b) PDC, CH_2Cl_2 , HOAc (cat.), 4-Å sieves; (c) $\text{Ph}_3\text{P}=\text{CH-EWG}$, CH_2Cl_2 .

(11) General procedure: A solution of the ketone in benzene (0.10 M) with AIBN (0.1 equiv) and tributyltin hydride (3.0 equiv) was carefully degassed with argon and heated to 80 °C (bath temperature). After 5-8 h, thin-layer chromatography indicated that starting diene had been consumed. The reaction was quenched with water and extracted with ether. The organic layers were dried and concentrated, and the crude oil was subjected to flash chromatography with ether-hexanes to remove the tin byproducts and isolate the desired cyclic products.

can likely be attributed to the reversibility of the cyclization and the decreased availability of *n*-Bu₃SnH.

Two additional experiments were performed which clearly establish the presence of the stannyl enolate. In each, the one-electron or radical reactivity of the allylic *O*-stannyl ketyl from **6** was induced to cyclize under the anti-selective dilute reaction conditions in experiment 3 shown in Table II. The resultant stannyl enolate was then immediately quenched with either Br₂ or D₂O¹² to produce a ca. 2:1 mixture of **17** as shown in Scheme IV. These results indicate that the one-electron reactivity in the allylic *O*-stannyl ketyl can be isolated from the two-electron reactivity by sequential transformations; moreover, by the correct choice of experiment, both types of reactivity can be achieved.

In summary, these studies illustrate that an α,β -unsaturated ketone can function as a precursor to an allylic *O*-stannyl ketyl which permits anti-selective β -coupling cyclizations with a tethered activated alkene. The intermediates in the reaction display a dichotomy of one- and two-electron reactivity.

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Supplementary Material Available: General procedure for the intramolecular β -coupling of activated olefins, spectral data for compounds **6**-**17**, and difference NOE data for **14** (4 pages). Ordering information is given on any current masthead page.

(12) Deuterium incorporation was >85% as calculated by ¹H NMR integration of the methylene protons.

Synthesis and X-ray Structure of the First Dicoordinate Dialkylstannylene That Is Monomeric in the Solid State¹

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Synthesis and characterization of stable organostannylenes have presented a fascinating challenge in the chemistry of low-valent group 14 organometallic compounds.² Whereas, very recently, the first monomeric dialkyl- and diarylstannylenes, 2-pyridyl-bis(trimethylsilyl)methyl-substituted stannylenes³ and bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene,⁴ have been synthesized and characterized by X-ray crystallography, these stannylenes are stabilized by intramolecular contacts between the tin atom and neighboring nitrogen or fluorine atoms.⁵ We report herein

(1) Chemistry of Organosilicon Compounds. 287.

(2) For reviews, see: (a) Lickiss, P. D. *Chemistry of Tin*; Harrison, P. G., Ed.; Blackie: Glasgow and London, 1989; Chapter 7. (b) Lappert, M. F. *Rev. Silicon, Germanium, Tin Lead Compd.* 1986, 9, 129.

(3) Engelhardt, L. M.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* 1988, 336.

(4) (a) Bigwood, M. P.; Corvan, P. J.; Zuckermann, J. J. *J. Am. Chem. Soc.* 1981, 103, 7643. (b) Grützmacher, H.; Pritzkow, H.; Edelmann, F. T. *Organometallics* 1991, 10, 23.

(5) Several amino,^{6a} alkoxy,^{6b,c} and arylthio-substituted^{6d} stannylenes have been revealed by X-ray crystallography to be monomeric in crystals in which the tin has the coordination number of 2. The divalent tin would be stabilized by the effects of electronegativity of the ligand atoms and by the donation of the lone-pair electrons to the vacant 5p π orbital of the tin.