One- and Two-Electron Reactions from the Rearrangement of α-Ketocyclopropanes by *O*-Stannyl Ketyls

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Abstract: This work summarizes an investigation of the bifunctional reactions of tin(IV) enolates and radicals derived from the cleavage rearrangement of ketocyclopropanes with tributyltin hydride. The intermediates provide an unparalleled dual reactivity in synthesis, allowing for independent transformations with both electrophiles and radicophiles. Reactions of the enolate with aldehydes led to aldol products in diastereoselectivities up to 20:1 favoring the *erythro* product. Reactions with alkyl halides were also successful, constructing new carbon−carbon bonds by a nucleophilic displacement reaction. These reactions provide a neutral, mild, and novel alternative to the classical methods of ketone enolate alkylation performed with hindered bases. Finally, the radical portion of the cleaved intermediates, separated from the enolate by a methylene unit, was reacted with allylstannanes to prepare new γ-carbon bonds to an allyl unit. Overall, these new trialkyltin-associated radical anion intermediates allow entry into the rapidly developing manifold of one- and two-electron reactions.

Introduction

α-Ketocyclopropanes are generally not recognized by the synthetic community to be useful as a free radical precursor. However, the reaction of tributyltin hydride with this functionality led to a radical rearrangement discovered by Peryere over 25 years ago.[1,2] Although this rearrangement was originally just a mechanistic curiosity, potentially useful intermediates involving a tin(IV) enolate and a radical separated by a methylene unit can be readily obtained. After those seminal studies, further investigations of these promising intermediates have not appeared. An obvious extension of this work would involve two-electron reactions by quenching the tin(IV) enolate with electrophilic partners which could form new carbon−carbon bonds.[3] Moreover, one-electron elaborations with radicophiles such as allyltributylstannane also seemed promising and appeared to have not been examined in any synthetic applications.[4] The dualism in reactions of bifunctional intermediates such as radical anions has become an important goal in recent synthetic organic chemistry, and it is hoped that this work will further extend the utility of these species in one- and two-electron transformations.[5−7]

The reaction used to prepare the enolate and radical reactive intermediates involves the tributyltin radical cleavage of a cyclopropyl ketone, as shown in the synthetic sequence of **1** → **4** (Scheme 1). Initial formation of the *O*-stannyl ketyl **2**, followed by ring scission (**3**), prepares the tin(IV) enolate **4** after transfer of the R group. The enolates were reacted with aldehyde or alkyl halide electrophiles (E^+), as in the transformation of **4** → **5**, to examine the scope and stereochemical consequences of the two-electron reaction sequence. The one-pot process provides a useful one-electron alternative to the classical methods of ketone enolate alkylation performed with hindered bases such as LDA. Radical reactions with allyltributylstannane, as in the transformation of **3** → **4**, were also examined.[4] These transformations take advantage of the radical character in the bifunctional intermediate **3**.

Results and Discussion

The first reactions to be studied involved simple quenching of the tin(IV) enolate with aldehydes, as shown in Scheme 2. This reaction was run with tin hydride and a suitable cyclopropyl ketone under standard free radical conditions, and after TLC indicated consumption of the starting substrate, an aldehyde was added to the pot. Three observations about this reaction were readily apparent. First, if the cyclopropane ring is substituted with a radical-stabilizing function, such as a phenyl

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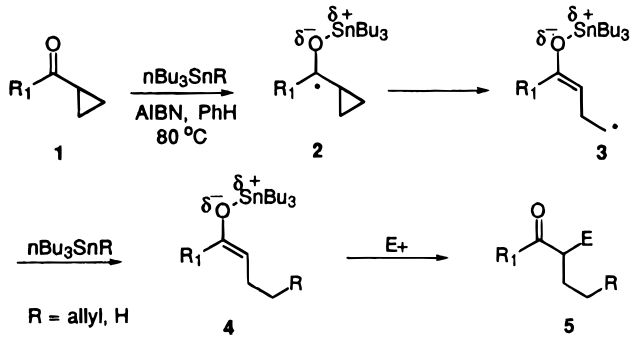
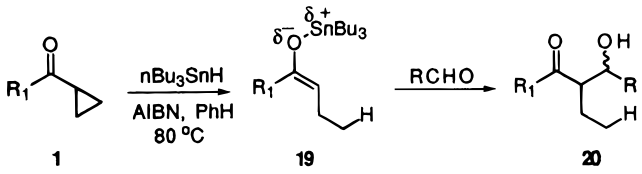
Scheme 1



Scheme 2



group, then it should be possible to selectively favor cleavage of one bond over the other. Second, two carbons in the cyclopropane ring become an appendage on the main backbone between the alcohol and the ketone. Third, two adjacent stereocenters are present in the products, affording the possibility of two diastereomers, the *erythro*- and *threo*-aldols.

Several results have been collected in Table 1. The aldol reaction appears to function well in the unconventional benzene solvent. In most cases the yields are quite good; however, the modest yield for the non-aryl ketocyclopropane **16** is not clear; the intermediate tin enolate appears to have reduced reactivity toward benzaldehyde. Ketocyclopropane **11** was utilized in an effort to study the effects of selective bond scission. The phenyl-stabilized radical intermediate formed from **11** was clearly what led to products, while the other bond cleavage was not observed even in minor products.

Also of interest was the major *erythro*-aldol formed in the reaction. Because tin(IV) enolates do not likely react in a cyclic chelated Zimmerman−Traxler transition state, particularly at or above ambient temperature, an extended transition state is proposed for the aldol, shown in Scheme 3.[8a] A related open transition state for aldol reactions of tributyltin(IV) enolates leading to the *erythro*-diastereomer has been proposed by Shibata.[3] The *Z*-isomer of the tin(IV) enolate bearing the aryl substituent should be preferred.[8b] Transition state **21** places the aldehyde R in a less-hindered environment when compared with **23**, leading to a predominance of the *erythro*-aldol. Particularly noteworthy is the 20:1 ratio of **7** to **8**. The simple diastereoselectivity is synthetically useful in several examples. Lower reaction temperatures were not practical due to the freezing point of benzene.

The stereochemical assignments (*erythro* or *threo*) were made by ^{1}H NMR, examining related aldol products and applying the $J_{threo} > J_{erythro}$ relationship.[9] For the major product, the coupling constant between the carbinol proton and the methine proton was ∼4−5 Hz; for the minor product, the coupling constant was ∼7−8 Hz. This assignment was further confirmed by ^{13}C NMR spectra. According to Heathcock's earlier studies, the carbinol resonance of *erythro*-*β*-hydroxycarbonyl compounds should be at 71.6−78.1 ppm and that of *threo*-isomer should be higher at 74.0−82.5 ppm.[10] For example, in Table 1, entry 2, the carbinol of the major *erythro* product **9** appeared at 73.8 ppm, while the carbinol of the minor *threo* product **10** was at 75.6 ppm. The *erythro* assignment for all major products was confirmed using these complementary methods.

The tin(IV) enolate, formed by the fragmentation of the α-ketocyclopropane, also was reacted with primary and allylic alkyl iodides, as shown in Scheme 4. To facilitate the reaction, 5 equiv of HMPA was added along with the alkyl halide. Previous studies in our laboratories have demonstrated that this is an optimum amount of HMPA to use in tin(IV) enolate alkylations.[6j] A collection of several results have been gathered in Table 2. All yields were synthetically useful for this mild transformation. In most cases overnight reflux was required. One limitation to this method is that only reactive alkyl halides, such as primary and activated allylic iodides, could be used, due to the reduced nucleophilicity of the intermediate tin enolate.[6j]

Next, the radical portion of the fragmented intermediates was reacted with allylstannanes to prepare a new carbon−carbon bond to an allyl unit. Related reactions using allyltributyltin have been systematically studied in some detail since Migita and Pereyre first reported organohalides undergo this free radical transformation.[11,12] Although numerous free radical reactions with allyltributylstannanes have been examined using halide, phenyl selenide, sulfide, and other precursors,[13] we could not find studies using ketocyclopropanes as starting substrates.

It was hoped that the propagation steps in these reactions would follow the sequence shown in Scheme 5. Initiation with AIBN forms the tributyltin radical from

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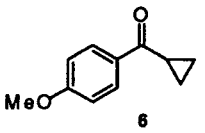
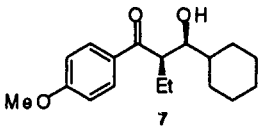
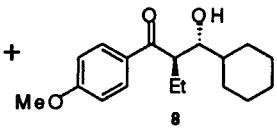
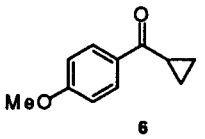
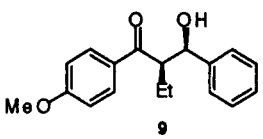
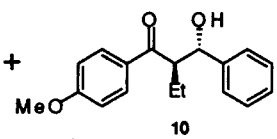
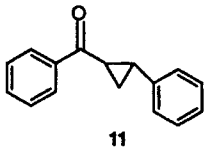
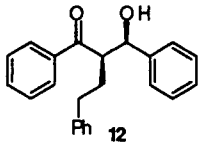
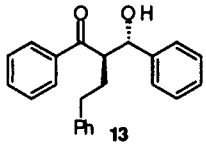
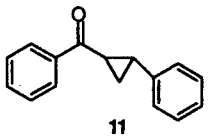
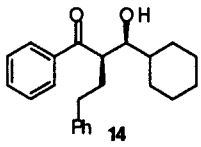
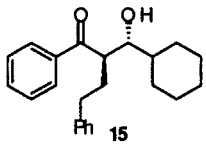
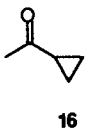
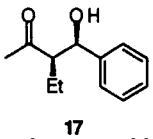
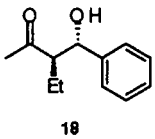
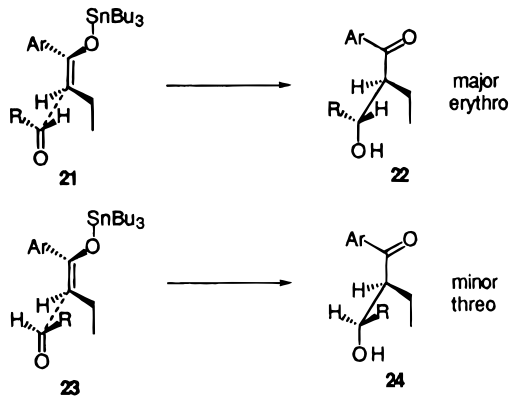
Table 1. Aldol Reactions of α-Ketocyclopropanes

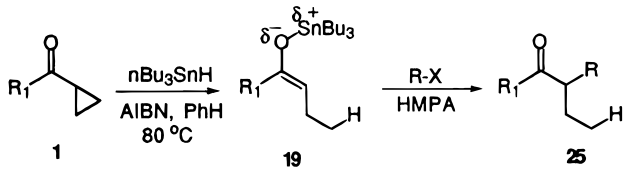
entry	α-ketocyclopropane	aldehyde[a]	aldol products	ratio[b] erythro : threo	yield (%)
1	 **6**	A	 **7** +  **8**	20 : 1	92
2	 **6**	B	 **9** +  **10**	4.4 : 1	97
3	 **11**	B	 **12** +  **13**	7 : 1	73
4	 **11**	A	 **14** +  **15**	8 : 1	92
5	 **16**	B	 **17**  **18**	3 : 1	35

[a] A = cyclohexanecarboxaldehyde, B = benzaldehyde. [b] Ratios determined by ^{1}H NMR integration.

Scheme 3



Scheme 4

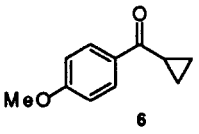
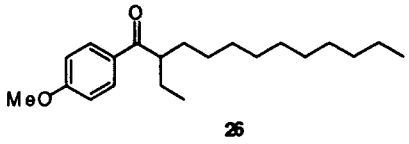
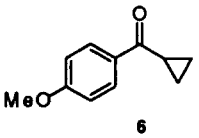
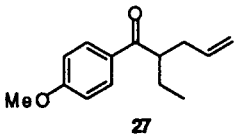
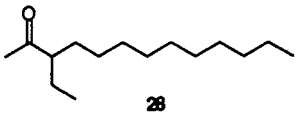
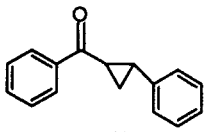
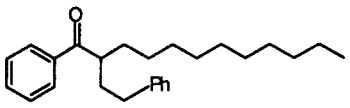
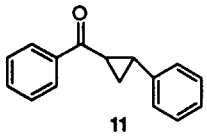
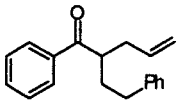


allyltributyltin and sets the propagation process in motion. The tin radical adds to the carbonyl of cyclopropyl ketone **1**, giving *O*-stannyl ketyl species **2**. The cyclopropane fragments to afford enolate radical **3**. Allyltributyltin adds an allyl unit through an S_H2' substitution and regenerates tributyltin radical to continue the chain reaction. Fragmentation−allylation product **31** is thus produced. This reaction expands the scope of *O*-stannyl ketyl-promoted cyclopropane fragmentations, allowing a combination of this work with allyltributyltin chemistry.

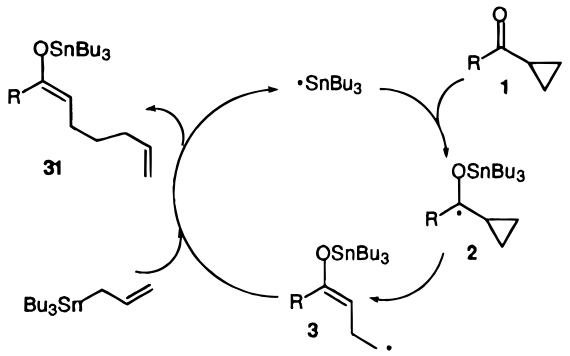
Cyclopropyl ketone **6** was first used to examine the fragmentation−allylation reaction. Refluxing with benzene and allyltributyltin (2 equiv) for several hours produced the desired product **32**, isolated in 50% yield based on recovered **6**, as shown in Scheme 6. Although the first example was only modestly successful, a second example with tricyclic ketone **33**[6i] as a starting substrate underwent excellent fragmentation−allylation, as shown in Scheme 7. The desired allylation product **35** was isolated as a single diastereomer (>50:1) in 94% yield. The increase in yield in this case can probably be attributed to the increase in release of strain energy during the fragmentation.

Several interesting aspects of these reactions are worth noting. First, selective cleavage of the cyclopropane bond leading to the ester-stabilized radical center was observed in Scheme 7, likely as a result of thermodynamic control.[6f] Even though there is better orbital overlap with the ketyl carbon, the kinetically controlled cleavage of the other cyclopropane bond did not predominate and no allyl transfer from this alternate mode of cyclopropane cleavage was observed. Moreover, the high diastereoselectivity in **35** might be rationalized by the steric differences between the faces of the radical center in intermediate **34** for approaching the allyltributyltin molecule. The face bearing the tin(IV) enolate is less hindered due to the presence of two sp^2 carbons. The stereochemistry of **34** was confirmed by NOE difference NMR. Finally this interesting free radical method constructed a new carbon−carbon bond at the γ-position, relative to the carbonyl.

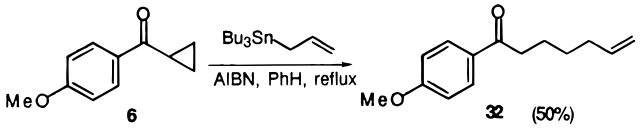
Table 2 Alkylation Reactions of α-Ketocyclopropanes

entry	α–ketocyclopropane	alkyl halide	product	yield (%)
1	 **6**		 **26**	95
2	 **6**		 **27**	86
3	 **16**		 **28**	67
4	 **11**		 **29**	79
5	 **11**		 **30**	97

Scheme 5



Scheme 6

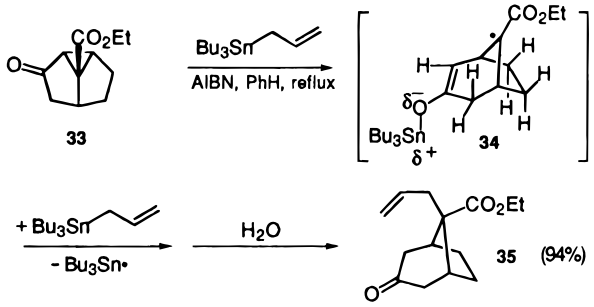


This type of bond construction using nonnucleophilic methods with a cyclopropyl ketone is difficult to achieve.

Conclusion

The fragmentation reaction of a cyclopropyl ketone with tributyltin radical produces a tin(IV) enolate separated from a carbon-centered radical by a methylene unit. These distinct entities allow for reactions with both electrophiles and radicophiles. Primary and activated alkyl iodides readily react with the tin(IV) enolate, affording a new method to form carbon−carbon bonds. Aldehydes reacted with the enolate to produce aldol-type products with stereoselectivities up to 20:1, favoring the *erythro*-diastereomer. The radical center also underwent reactions with allyltributylstannane, with one example giving a diastereoselectivity of 50:1. Overall, these new trialkyltin-associated radical anion intermediates allow entry into the rapidly developing manifold of one- and two-electron reactions.

Scheme 7



Experimental Section

General. Melting points were determined on a capillary melting point apparatus and are uncorrected. Infrared spectra are reported in wavenumbers (cm^{-1}). Chemical shifts for NMR are reported in ppm downfield (δ) relative to tetramethylsilane as an internal standard in chloroform. All product ratios were determined by ^1H NMR integration of the mixture of aldols.

All reactions were run under an inert atmosphere of argon using flame-dried apparatus. All reactions were monitored by thin-layer chromatography (TLC) and judged complete when starting material was no longer visible in the reaction mixture as spotted on TLC. All yields reported refer to isolated material judged to be homogeneous by thin-layer chromatog-

raphy and NMR spectroscopy. Temperatures above and below ambient temperature refer to bath temperatures unless otherwise stated. Solvents and anhydrous reagents were dried according to established procedures by distillation under nitrogen from an appropriate drying agent: ether, benzene, and THF from benzophenone ketyl; dichloromethane from CaH_2. Other solvents were used as received from the manufacturer. Analytical TLC was performed using precoated silica gel plates (0.25 mm) using phosphomolybdic acid in ethanol as an indicator. Column chromatography was performed using flash silica gel (230−400 mesh). Compounds **6** and **16** were commercially available.

General Procedure for Cyclopropane Fragmentation−Aldol Reaction. A cyclopropyl ketone (1 equiv), tributyltin hydride (1.5 equiv), and AIBN (0.3 equiv) were dissolved in benzene (0.3 M) and degassed for 20 min with a stream of Ar. The reaction mixture was then refluxed until the ketone was consumed by TLC (∼2 h). The reaction flask was cooled to room temperature, and an aldehyde (3 equiv) was added. The reaction was allowed to stir for 8 h. To the reaction mixture were added DBU (1.8 equiv) and 2−3 drops of water.[14] A solution of iodine in ethyl ether was added dropwise by a pipet, until the iodine orange color permanently persisted. The mixture was suctioned through a silica plug in a coarse fritted funnel using copious amount of ether. The ether solution was rotovapped, and the residue was subjected to column chromatography to afford the aldol products.

General Procedure for Cyclopropane Fragmentation−Alkylation Reaction. A cyclopropyl ketone (1 equiv), tributyltin hydride (1.5 equiv), and AIBN (0.3 equiv) were dissolved in benzene (0.3 M) and degassed for 20 min with Ar. The reaction mixture was then refluxed until the ketone was consumed by TLC (∼2 h). The reaction flask was cooled to room temperature, and HMPA (5.0 equiv) was added. The mixture was stirred for 3−5 min, and an alkyl halide (4.0 equiv) was added. The mixture was refluxed for 8 h Workup with DBU and iodine and chromatography identical with the procedure above gave the desired alkylated products.[14]

Phenyl(*trans*-2-phenylcyclopropyl)methanone (11).[15] Solid NaH (60% in oil, 231 mg, 5.77 mmol) was placed in a 3-necked flask, washed with *n*-pentane, and fully pumped to dryness. Trimethyloxosulfonium iodide (1270 mg, 5.77 mmol) was added, and DMSO (10 mL) was added dropwise to the solid mixture through an addition funnel. After hydrogen evolution, the milky solution turned clear and was stirred for 15 min. *trans*-Chalcone (1 mg, 4.81 mmol) was added. The mixture was stirred for 20 h, and the reaction was quenched with water. The mixture was extracted with ether, and the organic layers were dried, rotovapped, and chromatographed to give **11** (1080 mg, quantitative) as a white solid: R_f (1:3 ether/hexane) 0.48; ^{1}H NMR δ 8.01−7.98 (m, 2H), 7.59−7.56 (m, 1H), 7.49−7.43 (m, 2H), 7.35−7.29 (m, 2H), 7.25−7.22 (m, 1H), 7.21−7.17 (m, 2H), 2.91 (m, 1H), 2.70 (m, 1H), 1.93 (m, 1H), 1.56 (m, 1H); ^{13}C NMR δ 198.5, 140.5, 137.8, 132.9, 128.5 (4C), 128.1 (2C), 126.6 (2C), 126.2, 30.0, 29.3, 19.2; HRMS for $C_{16}H_{14}O$ calcd 222.1045, found 222.1056.

Aldols 7 and 8: R_f (1:1 ether/hexane) 0.36. For *erythro*-**7**: ^{1}H NMR δ 7.96 (d, J = 9 Hz, 2H), 6.96 (d, J = 9 Hz, 2H), 3.87 (s, 3H), 3.65−3.55 (m, 2H), 2.02−1.87 (m, 2H), 1.82−1.66 (m, 4H), 1.53−0.84 (m, 11H); ^{13}C NMR δ 204.1 (s), 163.7 (s), 130.6 (d, 2C), 130.3 (s), 113.8 (d, 2C), 76.0 (d), 55.3 (d), 48.0 (d), 40.6 (d), 29.4 (t), 28.8 (t), 26.2 (t), 26.0 (t), 25.8 (t), 19.7 (t), 12.3 (q). For *threo*-**8**: ^{13}C NMR δ 77.3 for the carbinol. HRMS for $C_{18}H_{26}O_3$ calcd 290.1882, found 290.1814.

Aldols 9 and 10: R_f (1:1 ether/hexane) 0.24. For *erythro*-**9**: ^{1}H NMR δ 7.89 (d, J = 9 Hz, 2H), 7.44−7.17 (m, 5H), 6.90 (d, J = 9 Hz, 2H), 5.05 (d, J = 4.5 Hz, 1H), 3.84 (s, 3H), 3.67 (m, 1H), 2.58 (s, 1H), 1.43−1.31 (m, 2H), 0.76 (t, J = 7 Hz, 3H); ^{13}C NMR δ 203.7, 163.8, 142.1, 130.6 (2C), 130.0, 128.1 (2C), 127.2, 126.1 (2C), 113.8 (2C), 73.8, 55.4, 53.5, 20.4, 12.1. For *threo*-**10**: ^{1}H NMR δ 4.99 (d, J = 5.9 Hz) for the carbinol proton; ^{13}C NMR δ 75.6 for the carbinol. HRMS for $C_{18}H_{20}O_3$ M + H calcd 285.1491, found 285.1463.

Aldols 12 and 13: R_f (1:2 ether/hexane) 0.38. For *erythro*-**12**: ^{1}H NMR δ 7.75 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.39−7.11 (m, 10H), 6.93 (d, J = 6.3 Hz, 2H), 5.05 (d, J = 2.7 Hz, 1H), 3.79 (m, 1H), 3.35 (d, J = 2.4 Hz, 1H), 2.53−2.28 (m, 2H), 2.22−2.03 (m, 2H); ^{13}C NMR δ 204.8 (s), 141.8 (s), 141.3 (s), 136.9 (s), 133.4 (d), 128.6 (d, 2C), 128.3 (d, 8C), 127.5 (d), 126.1 (d, 2C), 125.9 (d), 73.7 (d), 52.0 (d), 33.6 (t), 28.4 (t). For *threo*-**13**: ^{1}H NMR δ 5.00 (d, J = 6.3 Hz) for the carbinol proton; ^{13}C NMR δ 75.8 for the carbinol. HRMS for $C_{23}H_{22}O_2$ M + H, calcd 331.1698, found 331.1694.

Aldols 14 and 15: R_f (1:2 ether/hexane) 0.39. For *erythro*-**14**: ^{1}H NMR δ 7.76 (d, J = 7 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 7.5 Hz, 2H), 7.30−7.12 (m, 5H), 3.72 (m, 1H), 3.53 (m, 1H), 2.73−2.62 (m, 1H), 2.58 (d, J = 3 Hz, 1H), 2.49−2.25 (m, 2H), 2.02−1.92 (m, 2H), 1.78−1.36 (m, 10H); ^{13}C NMR δ 204.9 (s), 141.6 (s), 137.0 (s), 133.3 (d), 128.7 (d, 2C), 128.4 (d, 2C), 128.3 (d, 2C), 128.2 (d, 2C), 125.9 (d), 76.0 (d), 46.6 (d), 40.7 (d), 33.7 (t), 29.2 (t), 29.0 (t), 27.6 (t), 26.2 (t), 26.0 (t), 25.8 (t). For *threo*-**15**: ^{13}C NMR δ 77.0 for the carbinol. HRMS for $C_{23}H_{28}O_2$ M + H calcd 337.2168, found 337.2167.

Aldols 17 and 18: R_f (1:1 ether/hexane) 0.37. For *erythro*-**17**: ^{1}H NMR δ 7.29 (m, 5H), 4.79 (d, J = 6.3 Hz, 1H), 3.16 (s, 1H), 2.81 (m, 1H), 1.93 (s, 3H), 1.72 (m, 2H), 0.83 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 213.0 (s), 140.0 (s), 128.2 (d, 2C), 127.6 (d), 126.1 (d, 2C), 73.9 (d), 61.1 (d), 31.7 (q), 20.5 (t), 11.9 (q). For *threo*-**18**: ^{1}H NMR δ 4.72 (dd, J = 7.8, 3.6 Hz) for the carbinol proton; ^{13}C NMR δ 75.4 for the carbinol. HRMS for $C_{12}H_{16}O_2$ M + H calcd 193.1229, found 193.1227.

Ketone 26: R_f (1:1 ether/hexane) 0.87; ^{1}H NMR δ 7.87 (d, J = 9 Hz, 2H), 6.84 (d, J = 9 Hz, 2H), 3.75 (s, 3H), 3.22 (m, 1H), 1.66 (m, 2H), 1.52−1.35 (m, 2H), 1.13 (m, 16H), 0.79−0.74 (m, 6H); ^{13}C NMR δ 202.9, 163.2, 130.8, 130.3 (2C), 113.5 (2C), 55.2, 47.1, 32.1, 31.8, 29.8, 29.5 (2C), 29.4, 29.2, 27.5, 25.5, 22.6, 14.0, 11.8; HRMS for $C_{21}H_{34}O_2$ calcd 318.2559, found 318.2554.

Ketone 27: yield 86%; R_f (1:1 ether/hexane) 0.72; ^{1}H NMR δ 7.95 (d, J = 9 Hz, 2H), 6.94 (d, J = 7 Hz, 2H), 5.75 (m, 1H), 5.05−4.94 (m, 2H), 3.86 (s, 3H), 3.41 (m, 1H), 2.38 (m, 2H), 1.69 (m, 2H), 0.87 (t, J = 7 Hz, 3H); ^{13}C NMR δ 202.0, 163.3, 136.0, 130.4 (3C), 116.3, 113.7 (2C), 55.3, 46.8, 36.0, 25.0, 11.6; HRMS for $C_{14}H_{18}O_2$ calcd 218.1307, found 218.1304. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.92; H, 8.37.

Ketone 28: yield 67%; R_f (1:4 ether/hexane) 0.59; ^{1}H NMR δ 2.28 (m, 1H), 2.04 (s, 3H), 1.61−1.32 (m, 4H), 1.18 (m, 16H), 0.83−0.76 (m, 6H); ^{13}C NMR δ 212.9 (s), 54.8 (d), 31.8 (t), 31.2 (t), 29.7 (t), 29.5 (t, 2C), 29.4 (t), 29.3 (t), 28.6 (q), 27.4 (t), 24.5 (t), 22.6 (t), 14.0 (q), 11.7 (q); HRMS for $C_{15}H_{30}O$ M + H, calcd 227.2375, found 227.2382.

Ketone 29: yield 79%; R_f (1:4 ether/hexane) 0.69; ^{1}H NMR δ 7.78 (d, J = 7.2 Hz, 2H), 7.43 (t, J = 7 Hz, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.17−7.00 (m, 5H), 3.34 (m, 1H), 2.49 (m, 2H), 2.03 (m, 1H), 1.69 (m, 2H), 1.44 (m, 1H), 1.12 (m, 16H), 0.77 (t, J = 7 Hz, 3H); ^{13}C NMR δ 204.1 (s), 141.8 (s), 137.4 (s), 132.8 (d), 128.5 (d, 2C), 128.4 (d, 2C), 128.2 (d, 2C), 128.1 (d, 2C), 125.8 (d), 45.2 (d), 33.7 (t), 33.6 (t), 32.4 (t), 31.8 (t), 29.7 (t), 29.5 (t, 2C), 29.3 (t), 29.2 (t), 27.4 (t), 22.6 (t), 14.1 (q); HRMS for $C_{26}H_{36}O$ M + H, calcd 365.2844, found 365.2813.

Ketone 30: yield 97%; R_f (1:4 ether/hexane) 0.60; ^{1}H NMR δ 7.92 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.32−7.15 (m, 5H), 5.79 (m, 1H), 5.10−5.01 (m, 2H), 3.57 (m, 1H), 2.74−2.55 (m, 3H), 2.40−2.31 (m, 1H), 2.26−2.13 (m, 1H), 1.96−1.84 (m, 1H); ^{13}C NMR δ 203.1 (s), 141.6 (s), 137.1 (s), 135.4 (d), 132.9 (d), 128.6 (d, 2C), 128.4 (d, 2C), 128.3 (d, 2C), 128.2 (d, 2C), 125.9 (d), 116.8 (t), 44.9 (d), 36.3 (t), 33.3 (t), 33.2 (t); HRMS for $C_{19}H_{20}O$ M + H, calcd 265.1592, found 265.1592.

1-(4-Methoxyphenyl)hept-6-enone (32). A mixture of ketone **6** (200 mg, 1.14 mmol), allyltributyltin (1.7 mL, 5.68 mmol), and AIBN (186 mg, 1.14 mmol) in benzene (0.5 mL) was degassed with a stream of Ar for 10 min and heated at 80 °C for 24 h. Then, AIBN (186 mg, 1.14 mmol) was added, and the mixture was degassed again with Ar at room temperature for 10 min. The mixture was again heated at 80 °C for 24 h. The mixture was directly subjected to column chromatography to give unreacted **6** (105 mg) and **32** (59 mg, 24%; 50% if

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corrected with recovered **6**): R_f (1:3 ether/hexane) 0.47; ^{1}H NMR δ 7.94 (d, J = 9 Hz, 2H), 6.93 (d, J = 9 Hz, 2H), 5.82 (m, 1H), 5.05−4.94 (m, 2H), 3.87 (s, 3H), 2.91 (q, J = 7.5 Hz, 2H), 2.10 (q, J = 7 Hz, 2H), 1.75 (m, 2H), 1.48 (m, 2H); ^{13}C NMR δ 198.9, 163.3, 138.5, 130.3 (2C), 130.1, 114.5, 113.6 (2C), 55.4, 38.0, 33.6, 28.6, 24.0; HRMS for $C_{14}H_{18}O_2$ calcd 218.1307, found 218.1304.

8-Allyl-8-(ethoxycarbonyl)bicyclo[3.2.1]octan-3-one (35). A mixture of tricyclic ketone **54**[6i] (330 mg, 1.70 mmol), allyltributyltin (1.3 mL, 4.25 mmol), and AIBN (139 mg, 0.851 mmol) in benzene (1.7 mL) was degassed with argon for 15 min and refluxed for 16 h. The mixture was directly chromatographed to give the allylation product **35** (376 mg, 94%) as a clear oil: R_f (1:1 ether/hexane) 0.58; IR (KBr) 1720; ^{1}H NMR δ 5.70−5.57 (m, 1H), 4.99−4.97 (m, 1H), 4.97−4.91 (m, 1H), 4.09 (q, J = 7 Hz, 2H), 2.65 (d, J = 15 Hz, 2H), 2.37 (dd, J = 4.2 Hz, 2.7 Hz, 2H), 2.25 (d, J = 7 Hz, 2H), 2.13 (m, 2H), 1.91−1.87 (m, 2H), 1.44 (m, 2H), 1.17 (t, J = 7 Hz, 3H); ^{13}C NMR δ 212.0 (s), 173.8 (s), 133.0 (d), 118.0 (t), 60.4 (t), 58.5 (s), 47.6 (t, 2C), 39.3 (d, 2C), 27.2 (t, 3C), 14.3 (q); HRMS for $C_{14}H_{20}O_3$ M + H calcd 237.1491, found 237.1498.

Acknowledgment. We gratefully acknowledge support by the National Science Foundation (Grant CHE-9708139) for this work.

Supporting Information Available: Proton NMR spectra for compounds **7**−**15**, **17**, **18**, **26**, **28**−**30**, **32**, and **35** (12 pages). This material is contained in 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.

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