# Diastereoselective Manipulations of Bicyclo[*m*.1.0]alkane Derivatives. 4. Reactions of Nucleophiles with Bicyclo[*m*.1.0]alk-3-en-2-ones

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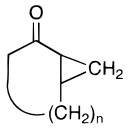
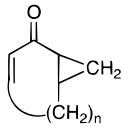
Enantiomerically enriched bicyclo[*m*.1.0]alk-3-en-2-ones possessing 8-, 12-, and 15-membered rings were prepared and subjected to additions of nucleophiles. 1,2-Additions of *n*-butyllithium were highly diastereoselective for all cyclopropyl enones examined. Reactions of (*Z*)-bicyclo[6.1.0]non-3-en-2-one and (*E*)-bicyclo[13.1.0]hexadec-3-en-2-one with dimethyloxosulfonium methylide were highly diastereoselective, while reaction of (*E*)-bicyclo[10.1.0]tridec-3-en-2-one with this reagent was not diastereoselective. In contrast, 1,4-additions of lithium diorganocuprates were highly diastereoselective for the 8- and 12-membered enones but were not diastereoselective for the 15-membered enone. All reactions were chemically efficient. The diastereoselectivities observed for 1,2-additions, which are thought to involve early transition states, can be rationalized by consideration of the low-energy conformations of each cyclopropyl enone. The diastereoselectivities observed for 1,4-additions, which may involve late transition states, do not correlate simply with the lowest energy conformations of these enones.

## Introduction

Carbocycles are frequently employed as templates in stereocontrolled organic synthesis. The reactivity of ring-bound functional groups can often be predicted with certainty for common rings[1] since the number of conformations is limited. Although medium and large rings can accommodate a greater variety of conformations, stereocontrolled manipulations are possible in cases where a product-determining conformational bias exists due to the presence of one or more stereogenic units.[2] We have developed an enantioselective synthesis of bicyclo[*m*.1.0]alkan-2-ones[3] **1** and have undertaken computational and synthetic studies to determine the suitability of these molecules for construction of natural products.[4] Of interest are bicyclo[*m*.1.0]alk-3-en-2-ones **2**. Such compounds might afford stereocontrol at multiple reactive centers on the ring. Furthermore, they present an opportunity to test further the utility of conformational analysis of medium and large carbocycles as a predictive tool for chemical reactivity. The conformational ensembles for the set of bicyclo[*m*.1.0]alk-3-en-2-ones **2** possessing cis ring fusion for $m = 3-14$ or trans ring fusion for $m = 7-14$ have been studied by computational methods.[5] In this paper, syntheses of representative enones **2** and nucleophilic 1,2- and 1,4-addition reactions of these molecules are presented and discussed.




**1**




**2**

## Syntheses of Bicyclo[*m*.1.0]alk-3-en-2-ones

α,β-Cyclopropyl α′,β′-enones employed in this study are depicted in Scheme 1 and include (*Z*)-(1*R*,8*S*)-bicyclo-[6.1.0]non-3-en-2-one (*Z*-**3**), (*Z*)-(1*S*,12*S*)-bicyclo[10.1.0]-tridec-3-en-2-one (*Z*-**4**), (*E*)-(1*S*,12*S*)-bicyclo[10.1.0]tridec-3-en-2-one (*E*-**4**), and (*E*)-(1*S*,15*S*)-bicyclo[13.1.0]hexadec-3-en-2-one (*E*-**5**). Enones **3**−**5** were prepared from the corresponding enantiomerically enriched bicyclo[*m*.1.0]-alkan-2-ones **1a**−**1c** via an α-phenylselenylation−oxidation−selenoxide elimination sequence.[6] Enone *Z*-**3** was obtained in 59% yield over three steps as the exclusive product from **1a**. Likewise, enone *E*-**5** was obtained in 80% yield from **1c**. However, a 1:20 mixture of enones *Z*-**4** and *E*-**4** was produced from **1b**. These isomers were easily separated by column chromatography and were assigned structures on the basis of the coupling constants observed for the vinylic protons in the $^1$H NMR spectra.

## Reactions of Bicyclo[*m*.1.0]alk-3-en-2-ones 3−5 with *n*-Butyllithium

On the basis of conformational modeling[5] and previous studies of nucleophilic 1,2-additions to bicyclo[*m*.1.0]-

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) For classification of rings by size, see: Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994; p 678.

(2) (a) Vedejs, E.; Dolphin, J. M.; Gapinski, D. M.; Mastalerz, H. In *Current Trends in Organic Synthesis*; Pergamon Press: Tokyo, Japan, 1982; pp 221−232. (b) Still, W. C. In *Current Trends in Organic Synthesis*; Pergamon Press: Tokyo, Japan, 1982; pp 233−246. (c) Vedejs, E. In *Studies in Natural Products Chemistry*; Atta-ur-Raman, Ed.; Elsevier: Amsterdam, 1991; Vol. 8; pp 205−218. (d) Neeland, E. G.; Sharadendu, A.; Weiler, L. *Tetrahedron Lett.* **1996**, *37*, 5069−5072. (e) Couturier, M.; Deslongchamps, P. *Synlett* **1996**, 1140−1142. (f) Nakajima, N.; Yonemitsu, O. in *Studies in Natural Products Chemistry*; Atta-ur-Raman, Ed.; Elsevier: Amsterdam, 1992; Vol. 11; pp 151−180. (g) Suginome, H.; Kondoh, T.; Gogonea, C.; Singh, V.; Goto, H.; Osawa, E. *J. Chem. Soc., Perkin Trans. 1* **1995**, 69−81.

(3) (a) Mash, E. A.; Math, S. K.; Arterburn, J. B. *J. Org. Chem.* **1989**, *54*, 4951−4953. (b) Mash, E. A.; Torok, D. S. *J. Org. Chem.* **1989**, *54*, 250−253. (c) Mash, E. A.; Nelson, K. A. *Tetrahedron* **1987**, *43*, 679−692. (d) Nelson, K. A.; Mash, E. A. *J. Org. Chem.* **1986**, *51*, 2721−2724. See also: (e) Yeh, S.-M.; Huang, L.-H.; Luh, T.-Y. *J. Org. Chem.* **1996**, *61*, 3906−3908.

(4) (a) Mash, E. A.; Nimkar, K. S.; Baron, J. A. *Tetrahedron* **1997**, *53*, 9043−9056. (b) Mash, E. A.; Gregg, T. M.; Kaczynski, M. A. *J. Org. Chem.* **1996**, *61*, 2743−2752.

(5) Mash, E. A.; Gregg, T. M.; Stahl, M. T. *J. Org. Chem.* **1997**, *62*, 3715−3721.

(6) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434−5447.

S0022-3263(97)01359-5 CCC: $14.00 

**Scheme 1**

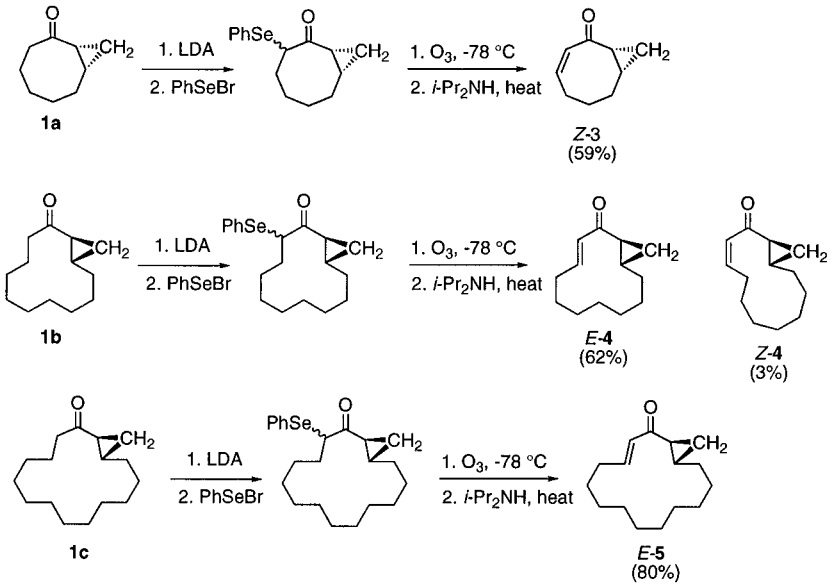
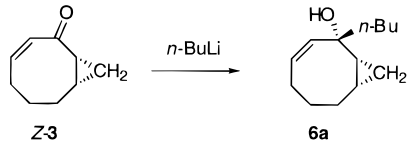
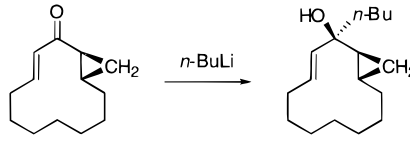
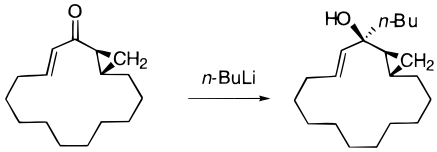



**Table 1. Additions of *n*-Butyllithium to Carbonyls of Bicyclo[*m*.1.0]alk-3-en-2-ones 3−5**

| Reaction | Product Yield, % | Product Ratio, a:b |
|---|---|---|
|  | 78 | 46:1 |
|  | 94 | >20:1 |
|  | 74 | >20:1 |

alkan-2-ones,[4b] high diastereoselectivities were anticipated for reactions of *Z*-**3**, *E*-**4**, and *E*-**5** with strong nucleophiles. Reaction of *n*-butyllithium with *Z*-**3** gave, in 78% yield, a 46:1 mixture of less and more polar adducts **6a** and **6b** (Table 1). Reaction of *n*-butyllithium with *E*-**4** and *E*-**5** produced adducts **7a** and **8a** in 94% and 74% yields, respectively, with no evidence of a second diastereomer in either case.[7]

For each cyclopropyl enone, conformational restrictions due to interactions of the cyclopropane, ketone, and alkene functional groups result in exposure of one face of the carbonyl to attack from the periphery of the ring. In conformers *Z*-**3**-1 and *Z*-**3**-3, the *Re* face of the carbonyl is exposed to attack, while approach at the *Si* face is blocked by transannular carbon and hydrogen atoms (Figure 1; the percentage given for each conformer is the percentage of the conformer population at 195 K). In conformer *Z*-**3**-2, attack at either carbonyl face appears possible. For enones *E*-**4** and *E*-**5**, the *Si* face of the carbonyl is exposed and the *Re* face is blocked in virtually all populated conformers (e.g., *E*-**4**-1 and *E*-**5**-1). As 1,2-additions of *n*-butyllithium were expected to proceed through early, reactant-like transition states, adducts arising from attack at the *Re* face of *Z*-**3** and at the *Si* faces of *E*-**4** and *E*-**5** were expected to predominate. Structures were tentatively assigned to the adducts on the basis of these considerations.[8]

(7) The signal-to-noise limit of detection was 20:1. For previous use of $^{13}C$ NMR in determination of diastereomer ratios, see: Hiemstra, H.; Wynberg, H. *Tetrahedron Lett.* **1977**, *18*, 2183-2186.

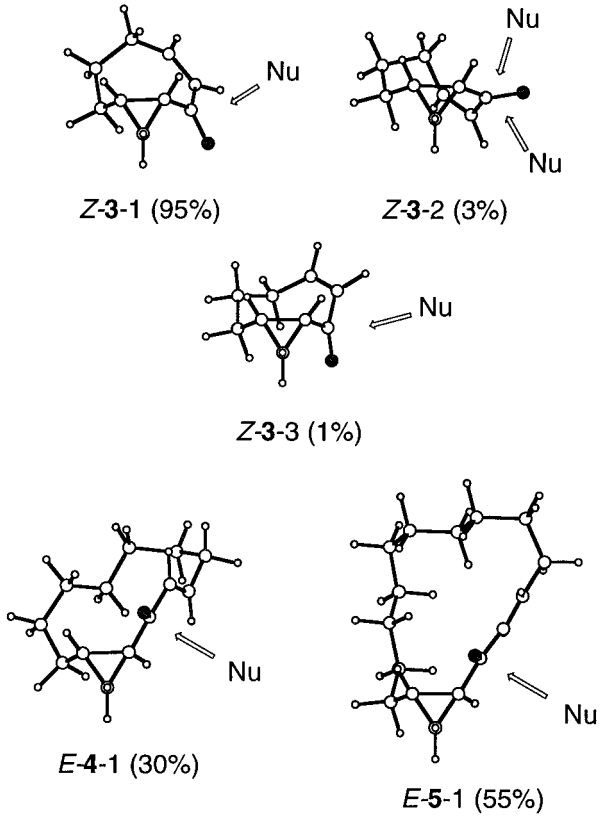
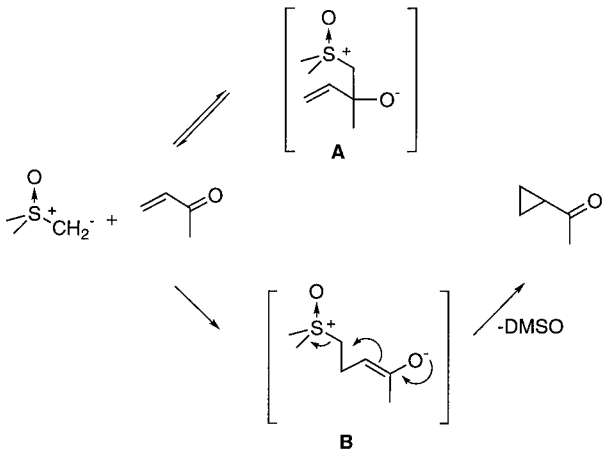



**Figure 1.** Nucleophilic 1,2-attack on the lowest energy conformers of *Z*-**3**, *E*-**4**, and *E*-**5**.

**Scheme 2**




## Reactions of Bicyclo[*m*.1.0]alk-3-en-2-ones 3−5 with Dimethyloxosulfonium Methylide

Reaction of dimethyloxosulfonium methylide[9] with an enone produces a cyclopropyl ketone (Scheme 2). Evidence suggests that in some cases formation of the betaine **B** can be rate-limiting and not appreciably reversible.[10,11] If so, then diastereoselectivity at the $\beta$ carbon will be determined in the transition state leading to **B**. To the degree that this transition state possesses starting material-like character, enone conformer populations should be useful for prediction of diastereoselectivity. Diastereoselectivity at the $\alpha$ carbon will then depend on the relative rates of $C_\alpha-C_\beta$ $\sigma$ bond rotation in **B** and collapse of **B** to product.

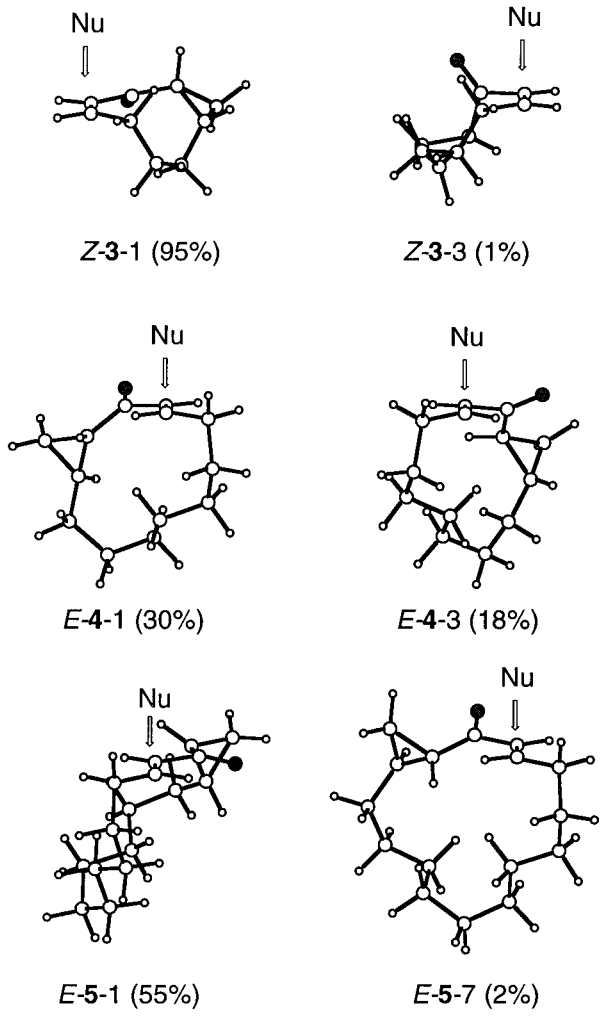


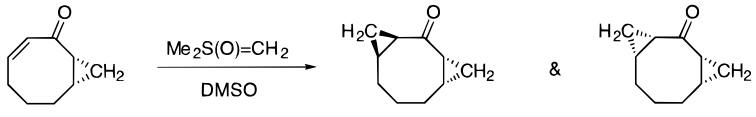
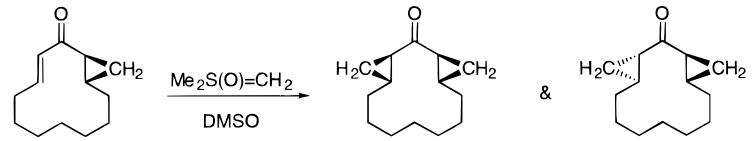
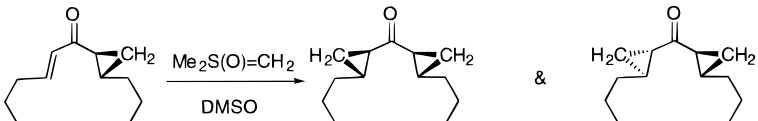

**Figure 2.** Nucleophilic attack by dimethyloxosulfonium methylide on low-energy conformers of *Z*-**3**, *E*-**4**, and *E*-**5**.

Reaction of enone *Z*-**3** with dimethyloxosulfonium methylide produced a single dicyclopropyl ketone diastereomer in 80% yield (Table 2). This compound was shown by $^1$H and $^{13}$C NMR to possess either 2-fold rotational symmetry (**12a**) or a plane of symmetry (**12b**). As the product was optically active, it was assigned structure **12a**. Reaction of dimethyloxosulfonium methylide with enones *E*-**4** and *E*-**5** gave two-component product mixtures in 71% and 86% yields, respectively. These mixtures were easily separated by silica gel column chromatography, and the dicyclopropyl ketone products were shown by $^1$H and $^{13}$C NMR to possess either a plane of symmetry (**13a** and **14a**) or 2-fold rotational symmetry (**13b** and **14b**). In each case, the less polar product was optically inactive, while the more polar product was optically active. The former were therefore assigned structures **13a** and **14a**, while the latter were assigned structures **13b** and **14b**. Diastereomers **13a** and **13b** were obtained in a 1.2:1 ratio, while **14a** and **14b** were obtained in a 16:1 ratio.[12]

(8) While a proof of structure for *n*-butyllithium adducts **6**−**8** would be desirable, all were obtained as oils and were unsuitable for crystallographic analysis. The conformational mobility of these compounds and the lack of both diastereomers of **7** and **8** for comparison purposes would compromise interpretation of NOE data.

(9) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353−1364.
(10) Johnson, C. R.; Schroeck, C. W.; Shanklin, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 7424−7431.
(11) Rocquet, F.; Sevin, A. *Bull. Soc. Chim. Fr.* **1974**, 881−887.

**Table 2. Reactions of Dimethyloxosulfonium Methylide with Bicyclo[*m*.1.0]alk-3-en-2-ones 3−5**

| Reaction | Product Yield, % | Product Ratio, a:b |
|---|---|---|
|  *Z*-**3** → **12a** & **12b** | 80 | >20:1 |
|  *E*-**4** → **13a** & **13b** | 71 | 1.2:1 |
|  *E*-**5** → **14a** & **14b** | 86 | 16:1 |

Product **12a** results from attack by the ylide at the *3Re,4Re* face of the alkene of enone *Z*-**3**. In conformers *Z*-**3**-1 (Figure 2) and *Z*-**3**-2 (not shown), this face is exposed to attack, while in conformer *Z*-**3**-3, the *3Si,4Si* face appears somewhat more exposed. Conformer *Z*-**3**-1 also possesses a nearly s-trans enone geometry, which should favor formation of the more stable trans enolate.

Good overlap of the carbonyl and the alkene occurs in all low-energy conformers of enone *E*-**4**. Both s-trans and s-cis enone geometries are significant in the conformer population (e.g., *E*-**4**-1 and *E*-**4**-3, Figure 2). In the former, the *3Si,4Re* face of the alkene is exposed to peripheral attack, while in the latter, the *3Re,4Si* face of the alkene is exposed. Attack on s-trans conformers similar to *E*-**4**-1 would likely produce trans enolates, whereas attack on s-cis conformers similar to that of *E*-**4**-3 would likely produce cis enolates. Although s-trans conformers are predominant (ca. 80%), roughly equal amounts of **13a** and **13b** were formed. This may mean that the conformer population differs quantitatively from that determined by molecular mechanics, that the transition state for attack by the ylide is not satisfactorily approximated by a model based on starting material geometries, or that betaine formation was appreciably reversible.

Good overlap of the carbonyl and the alkene also occurs in all low-energy conformers of enone *E*-**5**. Both s-trans and s-cis enone geometries are represented in the conformer population (e.g., *E*-**5**-1 and *E*-**5**-7, Figure 2), but in this case the s-cis geometry is greatly predominant (ca. 96%). Attack on s-cis conformers similar to *E*-**5**-1 would likely produce cis enolates, whereas attack on s-trans conformers similar to *E*-**5**-7 would likely produce trans enolates. The principal product, **14a**, results from attack by the ylide at the *3Re,4Si* face of enone *E*-**5**, which is exposed in the s-cis conformers. The minor product, **14b**, results from attack at the *3Si,4Re* face, which is exposed in the s-trans conformers.

The high diastereoselectivity observed for enone *E*-**5** demonstrates that the poor diastereoselectivity observed for *E*-**4** is not simply a trend toward poor selectivity with larger ring size. Changes in selectivity can be viewed simply as a consequence of switching from a ring size with a conformational preference for s-trans enone geometry (for *Z*-**3**), through a ring size where there is less of a preference for either geometry (for *E*-**4**), to a ring size which favors the s-cis geometry (for *E*-**5**) for a process under kinetic control. Alternatively, if significant enolate character must develop in the transition state leading to betaine **B**, factors governing enolate stability may help determine product ratios.[13] For some cyclopropyl enones **2**, enolate geometry is prescribed by ring size (as in *Z*-**3**). For others, the preferred enolate geometry may be most readily accommodated from a minority of conformers or from a majority of conformers. Predictions of diastereoselectivity based on starting material conformations may be useful when a single conformational motif for the cyclopropyl enone functional group array is shared by most of the conformer population, exposing one alkene face to peripheral attack, if the geometry favors development of the preferred enolate.

## Reactions of Bicyclo[*m*.1.0]alk-3-en-2-ones 3−5 with Lithium Diorganocuprates

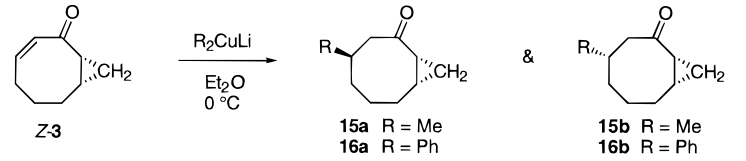
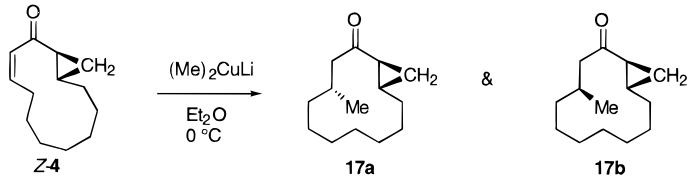
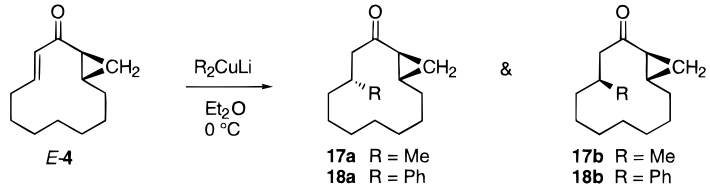
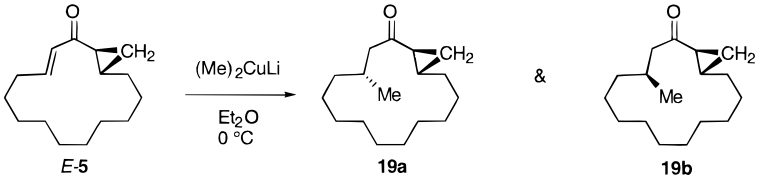
Reaction of a lithium diorganocuprate[14] with an α,β-unsaturated ketone produces a β-alkyl ketone via an

(12) Other diastereomers, while possible, were not observed. This implies that $C_\alpha-C_\beta$ σ bond rotation in the betaine intermediate was slower than and collapse to product.

(13) Neither experimental nor theoretical studies of the relative stabilities of trans and cis enolates derived from bicyclo[*m*.1.0]alkan-2-ones have been reported. In the absence of geometric constraints imposed by ring size, cis enolates are thermodynamically favored for dialkyl ketones. However, the difference in energy can be small. See: (a) ref 1, pp 897−905, and references therein. (b) Graham, R. J.; Weiler, L. *Tetrahedron Lett.* **1991**, *32*, 1027−1030. (c) Still, W. C.; Galynker, I. *Tetrahedron* **1981**, *37*, 3981−3996.

(14) For an overview, see: *Organocopper Reagents*; Taylor, R. J. K., Ed.; Oxford University Press: Oxford, 1994.

**Table 3. Reactions of Lithium Diorganocuprates with Bicyclo[*m*.1.0]alk-3-en-2-ones 3–5**

| Reaction | Product Yield, % | Product Ratio, a:b |
|---|---|---|
|  *Z*-**3** → **15a** R = Me, **16a** R = Ph & **15b** R = Me, **16b** R = Ph | **15**, 84<br>**16**, 95 | >20:1<br>>20:1 |
|  *Z*-**4** → **17a** & **17b** | **17**, 86 | <1:20 |
|  *E*-**4** → **17a** R = Me, **18a** R = Ph & **17b** R = Me, **18b** R = Ph | **17**, 90<br>**18**, 64 | >20:1<br>>20:1 |
|  *E*-**5** → **19a** & **19b** | **19**, 99 | 1.5:1 |

enolate. Despite much effort, the mechanism of this process is not well understood. Evidence supports the reversible formation of one or more complexes, which may or may not lie on the reaction path.[15] Whatever the mechanism, the transition state of the rate-determining step is not likely to resemble starting material.[16] Thus, it might be anticipated that knowledge of the enone conformations would be of little predictive value.

Reaction of enone *Z*-**3** with lithium dimethylcuprate gave a single product, **15a**, in 84% yield (Table 3).[7] Reaction of *Z*-**3** with lithium diphenylcuprate was similarly diastereoselective, producing **16a** in 95% yield. Reaction of enone *Z*-**4** with lithium dimethylcuprate also gave a single product, **17b**, in 86% yield. Enone *E*-**4** reacted with this cuprate to give only $\beta$-methyl ketone **17a** in 90% yield. Reaction of *E*-**4** with lithium diphenylcuprate produced **18a** in 64% yield. In contrast to the high diastereoselectivities observed with *Z*-**3**, *Z*-**4**, and *E*-**4**, reaction of *E*-**5** with lithium dimethylcuprate gave two products, **19a** and **19b**, in 60% and 39% yields, respectively.

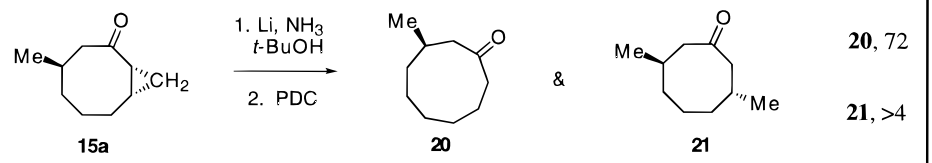
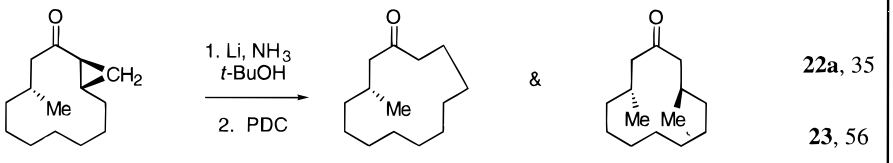
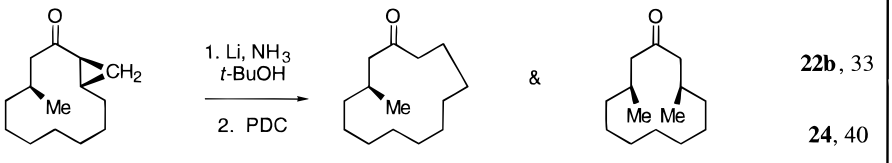
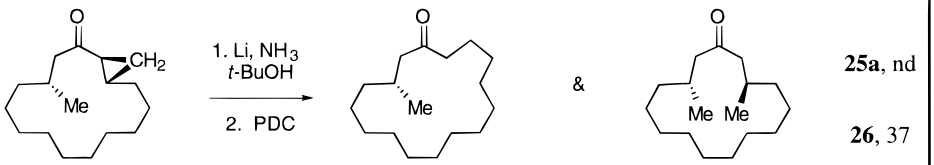
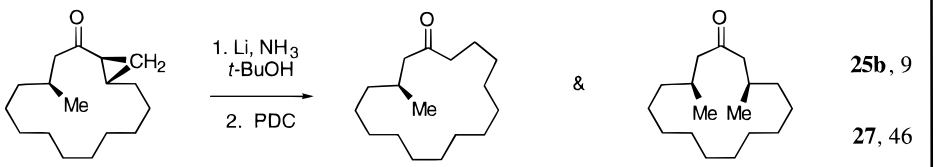
Products **15a**, **17a**, **17b**, **19a**, and **19b** were subjected to cyclopropane ring fragmentation using lithium metal in liquid ammonia, followed by oxidation of overreduced product with PDC, in attempts to establish the structures of these compounds and determine the facial selectivity for the 1,4-addition reactions in which they were produced (Table 4). In the case of **15a**, this sequence of reactions gave, in 76% yield, an inseparable mixture composed of an enantiomer of 3-methylcyclononanone, **20**, and trace amounts of an isomer of 3,7-dimethylcyclooctanone, **21**. The former product was unknown in the literature, and an insufficient amount of the latter product was available for determination of its optical rotation. Fortunately, ketone **16a** was crystalline. Single-crystal X-ray analysis determined that this ketone possessed the structure depicted in Table 3. The structure of **15a** is presumed by analogy to be as depicted in Table 3.

Reaction of **17a** with lithium in liquid ammonia produced, in 35% yield, an enantiomer of 3-methylcyclotetradecanone, **22a**, along with an isomer of 3,11-dimethylcyclotridecanone, obtained in 56% yield. Reaction of **17b** with lithium in liquid ammonia produced, in 33% yield, an enantiomer of 3-methylcyclotetradecanone, **22b**, along with a different isomer of 3,11-dimethylcyclotridecanone, obtained in 40% yield. The 3,11-dimethylcyclotridecanone products were shown by $^1$H and $^{13}$C NMR to possess either 2-fold rotational symmetry (**23**) or a plane of symmetry (**24**). The product derived from **17a** displayed optical activity and was assigned structure **23**, while the product derived from **17b** displayed no optical activity and was assigned structure **24**. The absolute configurations of **22a** and **22b** were assigned as 3*R* and 3*S*, respectively, by inference. Structure **18a** was

(15) (a) Corey, E. J.; Hannon, F. J. *Tetrahedron Lett.* **1990**, *31*, 1393–1396. (b) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6015–6018.

(16) Frantz, D. E.; Singleton, D. A.; Snyder, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 3383–3384 and references cited therein.

**Table 4. Reactions of 15a, 17a, 17b, 19a, and 19b with Lithium in Liquid Ammonia**

| Reaction | Yields, % |
|---|---|
|  **15a** → **20** & **21** | **20**, 72<br>**21**, >4 |
|  **17a** → **22a** & **23** | **22a**, 35<br>**23**, 56 |
|  **17b** → **22b** & **24** | **22b**, 33<br>**24**, 40 |
|  **19a** → **25a** & **26** | **25a**, nd<br>**26**, 37 |
|  **19b** → **25b** & **27** | **25b**, 9<br>**27**, 46 |

assigned to the 1,4-adduct of *E*-**4** with lithium diphenylcuprate by analogy with lithium dimethylcuprate adduct **17a**.

Reaction of **19a** with lithium in liquid ammonia produced, in 37% yield, an isomer of 3,14-dimethylcyclopentadecanone. Reaction of **19b** with lithium in liquid ammonia produced, in 55% yield, an inseparable 1:5 mixture of an enantiomer of 3-methylcyclohexadecanone, **25b**, and a different isomer of 3,14-dimethylcyclopentadecanone. The 3,14-dimethylcyclopentadecanone products were shown by $^{1}H$ and $^{13}C$ NMR to possess either 2-fold rotational symmetry (**26**) or a plane of symmetry (**27**). The product derived from **19a** displayed optical activity and was assigned structure **26**. The mixture derived from **19b** displayed nominal optical activity, due presumably to the 3-methylcyclohexadecanone contaminant,[17] and so the 3,14-dimethylcyclopentadecanone product derived from **19b** was assigned structure **27**.[18]

Products **15a** and **16a** result from selective transfer of a methyl or phenyl group by cuprate at the *3Re,4Re* face of the alkene of enone *Z*-**3**. In conformer *Z*-**3**-1 (Figure 2) this face is exposed to peripheral attack, and the enone geometry is nearly s-trans. This should favor formation of the obligate trans enolate. Product **17b** was produced by selective transfer of a methyl group at the *3Re,4Re* face of enone *Z*-**4**. This face is exposed to peripheral attack in the populated conformers of this enone, although the enone is severely twisted, compromising conjugative overlap (Figure 3). Products **17a** and **18a** result from selective transfer of a methyl or phenyl group by cuprate at the *3Si,4Re* face of *E*-**4**. As previously stated, both s-trans (ca. 80%, *3Si,4Re* face exposed) and s-cis (ca. 20%, *3Re,4Si* face exposed) enone geometries are significant in the conformer population for *E*-**4** (Figure 2). Nevertheless, high diastereoselectivity was observed. Products **19a** and **19b** were produced by transfer of a methyl group by cuprate at the *3Si,4Re* face and *3Re,4Si* face of enone *E*-**5**, respectively. Both s-trans (ca. 4%, *3Si,4Re* face exposed) and s-cis (ca. 96%, *3Re,-4Si* face exposed) enone geometries are represented in the conformer population (Figure 2). Good overlap of the carbonyl and the alkene occurs in the populated conform-

(17) The rotation of 3-methylcyclohexadecanone has not been reported.

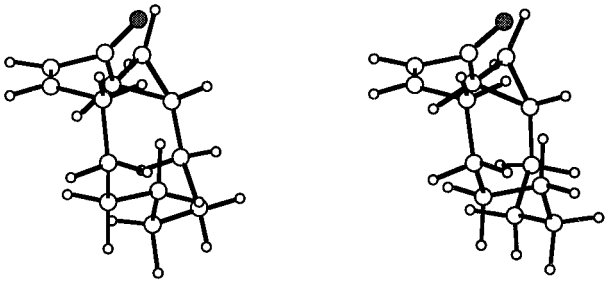



**Figure 3.** Low-energy conformers of *Z*-**4**.

ers of this enone. However, this 1,4-addition was remarkably nonselective.

Previously, lithium dimethylcuprate additions to several monocyclic medium and large enones have been shown to exhibit high levels of diastereoselection.[13c] The product ratios observed correlated with calculated enolate stabilities, which was taken as evidence for the involvement of late transition states in these reactions. The results from cuprate additions to cyclopropyl enones *Z*-**4**, *E*-**4**, and *E*-**5** are consistent with this assertion. Predictions of diastereoselectivity based on starting material conformations may be unreliable for bicyclo[*m*.1.0]alk-3-en-2-ones, even when a single conformational motif for the cyclopropyl enone functional group array is shared by most of the conformer population. Predictions based on calculation of the conformations and relative energies of the possible intermediate enolates should be more reliable. Examination of this assumption must await the development of suitable molecular mechanics parameters for the cyclopropyl enolate functional group array.[19]

## Experimental Section[20]

**(1*R*,8*S*)-Bicyclo[6.1.0]non-3-en-2-one (*Z*-3).** To a solution of LDA (2.2 mmol) in THF (5 mL) at −78 °C was added a solution of **1a**[3a] (238 mg, 1.7 mmol) in THF (2 mL) via cannula. After 30 min, a solution of PhSeBr, prepared by adding bromine (179 mg, 1.1 mmol) to diphenyl diselenide (354 mg, 1.1 mmol) dissolved in THF (1 mL), was added via syringe. The pale blue reaction mixture was poured into 0.5 N HCl (15 mL) and 50% (v/v) $Et_2O$/pentane (30 mL). The organic layer was separated, washed with water and a saturated $NaHCO_3$ solution, dried ($MgSO_4$), and filtered. Volatiles were removed, and the residual yellow oil was chromatographed on silica gel 60 (70−230 mesh, 125 g) eluted with 5% EtOAc/hexanes to give the corresponding α-phenylselenyl ketone, $R_f$ 0.20 (5% EtOAc/hexanes), as a colorless oil. Yield: 322 mg (1.1 mmol, 64%).

The above α-phenylselenyl ketone was dissolved in $CH_2Cl_2$ (5 mL) and the mixture cooled at −78 °C. Ozone in a stream of $O_2$ was bubbled through the solution until it became pale blue. Argon was then bubbled through the solution until the color disappeared. Diisopropylamine (110 mg, 1.1 mmol) was added, and the cold reaction mixture was rapidly transferred via cannula into a flask containing refluxing $CCl_4$ (10 mL) and diisopropylamine (60 mg, 0.55 mmol). The resulting yellow solution was cooled to rt, washed with 10% HCl and a 5% $NaHCO_3$ solution, dried ($MgSO_4$), and filtered. Volatiles were removed, and the residual yellow oil was chromatographed on silica gel 60 (240−400 mesh, 100 g) eluted with 0−20% $Et_2O$/pentanes to give 135 mg (1.0 mmol, 59%) of *Z*-**3**, $R_f$ 0.10 (10% $Et_2O$/pentane) as a pale yellow oil.

**Spectral data for *Z*-3:** $[\alpha]^{24}_D$ −73.4 (*c* 1.66, $CHCl_3$); IR (neat) $cm^{-1}$ 1647; $^1H$ NMR $\delta$ 0.45−0.55 (1, m), 0.92−1.13 (3, m), 1.40−1.58 (1, m), 1.68−1.97 (2, m), 2.08−2.33 (2, m), 3.09−3.28 (1, m), 6.08 (1, dd, $J$ = 11.9, 1.4 Hz), 6.27 (1, dt, $J$ = 11.9, 8.7 Hz); $^{13}C$ NMR $\delta$ 10.0, 16.1, 23.2, 25.0, 27.5, 133.7, 142.0, 201.7; HRMS (EI) calcd for $C_9H_{12}O$ 136.0888, found 136.0892.

**(*Z*)-(1*S*,12*S*)-Bicyclo[10.1.0]non-3-en-2-one (*Z*-4) and (*E*)-(1*S*,12*S*)-Bicyclo[10.1.0]non-3-en-2-one (*E*-4).** Enones *Z*-**4** and *E*-**4** were prepared from **1b**[3c] (572 mg, 2.9 mmol) in a manner similar to that described for the synthesis of *Z*-**3**. Chromatography of the crude product mixture on silica gel 60 (70−230 mesh, 100 g) eluted with 7−15% $Et_2O$/pentanes gave 27 mg of impure *Z*-**4**, $R_f$ 0.34 (10% EtOAc/hexanes), as a yellow solid contaminated with approximately 30% of **1b** (corrected yield 3% from **1b**) and 351 mg (1.8 mmol, 62%) of *E*-**4**, $R_f$ 0.28, as a crystalline solid, mp 30−33 °C. Spectral data appear in the Supporting Information.

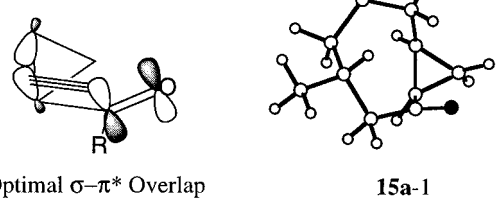
**(1*S*,15*S*)-Bicyclo[13.1.0]hexadec-3-en-2-one (*E*-5).** Enone *E*-**5** was prepared from **1c**[3d] (580 mg, 2.5 mmol) in a manner similar to that described for the synthesis of *Z*-**3**. Chromatography of the crude product on silica gel 60 (70−230 mesh, 100 g) eluted with 0−20% $Et_2O$/pentanes gave 467 mg (2.0 mmol, 80%) of *E*-**5**, $R_f$ 0.13 (5% EtOAc/hexanes), as a pale yellow oil. Spectral data appear in the Supporting Information.

**(1*R*,2*S*,8*S*)-2-Butylbicyclo[6.1.0]non-3-en-2-ol (6a) and (1*R*,2*R*,8*S*)-2-Butylbicyclo[6.1.0]non-3-en-2-ol (6b).** To a well-stirred solution of *n*-butyllithium (0.55 mL of a 1.2 M solution, 0.65 mmol) in THF (1 mL) at −78 °C was added a solution of enone *Z*-**3** (30 mg, 0.22 mmol) in THF (2 mL) via cannula. The reaction was allowed to warm to 0 °C over 2 h, at which time it was quenched by addition of a saturated aqueous $NH_4Cl$ solution (5 mL) and water (10 mL). The mixture was extracted with ether, the organic extracts were dried ($MgSO_4$) and filtered, and volatiles were removed. The residual oil was chromatographed on silica gel 60 (70−230 mesh, 25 g) eluted with 3% $Et_2O$/hexanes to give 32 mg (0.16 mmol, 76%) of the less polar diastereomer **6a**, $R_f$ 0.32 (10% EtOAc/hexanes), and 0.7 mg (0.004 mmol, ca. 2%) of the more polar diastereomer **6b**, $R_f$ 0.27, as colorless oils.

**Spectral data for 6a:** $[\alpha]^{25}_D$ −59.1 (*c* 1.59, $CHCl_3$); IR (neat) $cm^{-1}$ 3465 (br), 2999, 2953, 2929, 2858, 1455; $^1H$ NMR $\delta$ 0.50−0.78 (3, m), 0.91 (3, t, $J$ = 7.2 Hz), 1.10 (1, dt, $J$ = 9.2, 5.9 Hz), 1.22−1.77 (10, m), 1.89−2.07 (2, m), 2.72 (1, tdd, $J$ = 12.5, 7.6, 4.6 Hz), 5.38−5.52 (2, m); $^{13}C$ NMR $\delta$ 7.5, 14.1, 17.5, 23.2, 24.5, 24.6, 24.6, 26.1, 27.1, 46.4, 74.1, 126.8, 137.1; HRMS (EI) calcd for $C_{13}H_{22}O$ 194.1671, found 194.1665.

**Spectral data for 6b:** $^1H$ NMR $\delta$ −0.20 to −0.11 (1, m), 0.69−0.80 (2, m), 0.85−0.94 (1, m), 0.93 (3, t, $J$ = 7.2 Hz), 1.09−1.20 (1, m), 1.23−1.80 (9, m), 1.90−2.05 (2, m), 3.28 (1, dq, $J$ = 12.3, 6.5 Hz), 5.42 (1, td, $J$ = 11.0, 6.5 Hz), 5.68 (1, d, $J$ = 11.0 Hz).

(18) The variability in the ratios of ring-opened to ring-expanded products in the dissolving metal reductions of the different bicyclic ketones is notable (Table 4). Ring opening is thought to proceed by electron transfer to the carbonyl to give a radical anion, followed by subsequent cleavage of one of the α,β-cyclopropane bonds. The cyclopropane bond which breaks is normally the one with greater $\sigma-\pi^*$ overlap. Thus, the regioselectivity in this reaction is determined by the dominant conformers of the cyclopropyl−carbonyl torsion. Since electron transfer and ring opening, with the accompanying release of strain energy, is an extremely fast process, the ground state conformers of substrates may serve as useful models for predicting the regiochemical course of such reactions. As an illustration, reduction of **15a** proceeded to give almost exclusively ring-expanded product **20**. On consideration of the lowest energy conformer, **15a**-1, the dihedral angle from the carbonyl to the internal cyclopropane bond is 76°—very nearly optimal—while that from the carbonyl to the external bond is 7°.




Optimal σ−π* Overlap **15a**-1

(19) Molecular mechanics parameters are available for simple enolates, but the applicability of these parameters to enolates derived from bicyclo[*m*.1.0]alkan-2-ones is untested. Studies to clarify this point are in progress.

(20) For the General Experimental Section, see ref 4b.

**(1*S*,2*R*,12*S*)-2-Butylbicyclo[10.1.0]tridec-3-en-2-ol (7a).** From *n*-butyllithium (0.90 mmol) and *E*-**4** (58 mg, 0.30 mmol) was obtained 71 mg (0.21 mmol, 94%) of **7a**, $R_f$ 0.47 (10% EtOAc/hexanes), as a colorless oil. Spectral data appear in the Supporting Information.

**(1*S*,2*R*,15*S*)-2-Butylbicyclo[13.1.0]hexadec-3-en-2-ol (8a).** From *n*-butyllithium (0.85 mmol) and *E*-**5** (67 mg, 0.29 mmol) was obtained 61 mg (0.21 mmol, 74%) of **8a**, $R_f$ 0.42 (10% EtOAc/hexanes), as a colorless oil. Spectral data appear in the Supporting Information.

**(1*R*,3*R*,5*S*,9*S*)-Tricyclo[7.1.0.0$^{3,5}$]decan-2-one (12a).** Pentane-washed NaH (15 mg, 80% in oil, 0.50 mmol) was suspended in DMSO (0.5 mL) in a water bath at rt. After 30 min trimethyloxosulfonium iodide (88 mg, 0.40 mmol) was added. After 15 min, a solution of enone *Z*-**3** (49 mg, 0.36 mmol) in DMSO (1 mL) was added via cannula and the mixture was heated to 50 °C for 15 min. The mixture was cooled and quenched with water (10 mL), and the aqueous phase was extracted with pentane. The organic extracts were dried ($MgSO_4$) and filtered, and volatiles were removed. The residue was chromatographed on silica gel (240−400 mesh, 25 g) eluted with 20% $Et_2O$/pentane to give 44 mg (0.29 mmol, 80%) of **12a**, $R_f$ 0.20 (20% $Et_2O$/pentane), as a colorless liquid.

**Spectral data for 12a:** $[\alpha]^{24}_D$ +41 (*c* 2.18, $CHCl_3$); IR (neat) cm$^{-1}$ 1661; $^1$H NMR $\delta$ 1.00−1.42 (8, m), 1.55−1.70 (2, m), 1.79−1.90 (2, m), 2.02−2.15 (2, m); $^{13}$C NMR $\delta$ 12.4, 18.9, 24.9, 25.5, 27.5, 209.1; HRMS (EI) calcd for $C_{10}H_{14}O$ 150.1045, found 150.1045.

**(1*S*,3*R*,5*R*,13*S*)-Tricyclo[11.1.0.0$^{3,5}$]tetradecan-2-one (13a) and (1*S*,3*S*,5*S*,13*S*)-Tricyclo[11.1.0.0$^{3,5}$]tetradecan-2-one (13b).** Pentane-washed NaH (25 mg, 80% in oil, 0.83 mmol) was suspended in DMSO (1 mL) at rt, and trimethyloxosulfonium iodide (170 mg, 0.63 mmol) was added. After 30 min, a solution of enone *Z*-**4** (103 mg, 0.54 mmol) in DMSO (1 mL) was added via cannula while maintaining rt by means of a water bath. After 15 min the reaction was quenched with water (15 mL) and the reaction mixture was extracted with pentane. The organic extracts were dried ($MgSO_4$) and filtered, and volatiles were removed. The residue was chromatographed on silica gel (240−400 mesh, 30 g) eluted with 10% $Et_2O$/pentane to give 42 mg (0.20 mmol, 38%) of **13a**, $R_f$ 0.36 (10% EtOAc/hexanes), mp 76−80 °C, and 36 mg (0.17 mmol, 33%) of **13b**, $R_f$ 0.24, mp 54−58 °C.

**Spectral data for 13a:** $[\alpha]^{24}_D$ −0.1 (*c* 2.12, $CHCl_3$); IR (neat) cm$^{-1}$ 1669; $^1$H NMR $\delta$ 0.62−0.80 (4, m), 1.07−1.78 (14, m), 2.02−2.18 (4, m); $^{13}$C NMR $\delta$ 15.8, 28.0, 28.3, 29.5, 30.3, 30.5, 33.8, 209.8; HRMS (EI) calcd for $C_{14}H_{22}O$ 206.1671, found 206.1661.

**Spectral data for 13b:** $[\alpha]^{24}_D$ −78.0 (*c* 1.68, $CHCl_3$); IR (neat) cm$^{-1}$ 1661; $^1$H NMR $\delta$ 0.75−0.93 (4, m), 1.33−1.60 (16, m), 1.85−2.00 (2, m); $^{13}$C NMR $\delta$ 15.2, 24.8, 25.0, 25.9, 26.8, 28.4, 32.3, 208.9.

**(1*S*,3*R*,5*R*,16*S*)-Tricyclo[14.1.0.0$^{3,5}$]heptadecan-2-one (14a) and (1*S*,3*S*,5*S*,16*S*)-Tricyclo[14.1.0.0$^{3,5}$]heptadecan-2-one (14b).** From NaH (18 mg, 80% in oil, 0.60 mmol), trimethyloxosulfonium iodide (126 mg, 0.47 mmol), and enone *Z*-**5** (91 mg, 0.34 mmol) were obtained 78 mg (0.31 mmol, 81%) of **14a**, $R_f$ 0.42 (10% EtOAc/hexanes), mp 68−70 °C, and 5 mg (0.02 mmol, 5%) of **14b**, $R_f$ 0.29 after chromatography on silica gel (70−230 mesh, 110 g) eluted with 3−10% EtOAc/hexanes. Spectral data appear in the Supporting Information.

**(1*R*,4*R*,8*S*)-4-Methylbicyclo[6.1.0]nonan-2-one (15a).** To a slurry of CuI (140 mg, 0.76 mmol) in ether (2 mL) at 0 °C was added methyllithium (1.0 mL of a 1.4 M solution, 1.4 mmol) via syringe. After the solution was stirred for 15 min, a solution of the enone *Z*-**3** (48 mg, 0.35 mmol) in ether (2 mL) was added. After an additional 20 min of stirring, the reaction was quenched by addition of a saturated $NaHCO_3$ solution (5 mL). The mixture was diluted with water (5 mL) and extracted with ether. The organic extracts were dried ($MgSO_4$) and filtered, and volatiles were removed. The residue was chromatographed on silica gel 60 (240−400 mesh, 20 g) eluted with 10% $Et_2O$/pentane to give 45 mg (0.30 mmol, 84%) of **15a**, $R_f$ 0.31 (10% EtOAc/hexanes), as a colorless oil.

**Spectral data for 15a:** $[\alpha]^{23}_D$ +136 (*c* 2.11, $CHCl_3$); IR (neat) cm$^{-1}$ 1689; $^1$H NMR $\delta$ 0.57−0.83 (2, m), 1.00−1.28 (5, m), 1.32−1.70 (4, m), 1.78−1.96 (2, m), 2.13−2.25 (1, m), 2.27−2.36 (1, m), 2.43 (1, t, $J$ = 10.6 Hz); $^{13}$C NMR $\delta$ 8.1, 19.2, 24.4, 25.7, 27.5, 29.2, 32.4, 34.1, 59.3, 210.4.

**(1*R*,4*R*,8*S*)-4-Phenylbicyclo[6.1.0]nonan-2-one (16a).** From CuI (66 mg, 0.35 mmol), phenyllithium (0.65 mL of a 1.4 M solution, 0.91 mmol), and enone *Z*-**3** (31 mg, 0.23 mmol) was obtained 49 mg (0.22 mmol, 95%) of **16a**, $R_f$ 0.46 (20% EtOAc/hexanes), as white crystals, mp 82−85 °C, after chromatography on silica gel 60 (240−400 mesh) eluted with 10% $Et_2O$/hexanes. Spectral data appear in the Supporting Information.

The structure of **16a** was established by single-crystal X-ray analysis.[21]

**(1*S*,4*R*,12*S*)-4-Methylbicyclo[10.1.0]tridecan-2-one (17a).** From CuI (199 mg, 1.0 mmol), methyllithium (4.4 mL of a 0.45 M solution, 2.0 mmol), and enone *E*-**4** (95 mg, 0.50 mmol) was obtained 93 mg (0.45 mmol, 90%) of **17a**, $R_f$ 0.38 (10% EtOAc/hexanes), as a white crystalline solid, mp 50−53 °C, after chromatography on silica gel 60 (240−400 mesh) eluted with 10% $Et_2O$/pentane. Spectral data appear in the Supporting Information.

**(1*S*,4*S*,12*S*)-4-Methylbicyclo[10.1.0]tridecan-2-one (17b).** From CuI (93 mg, 0.50 mmol), methyllithium (2.0 mL of a 0.4 M solution, 0.80 mmol), and enone *Z*-**4** (19 mg, 0.10 mmol) was obtained 18 mg (0.090 mmol, 86%) of **17b**, $R_f$ 0.37 (10% EtOAc/hexanes), as a colorless solid after chromatography on silica gel 60 (70−230 mesh) eluted with 3% $Et_2O$/hexanes. Spectral data appear in the Supporting Information.

**(1*S*,4*R*,12*S*)-4-Phenylbicyclo[10.1.0]tridecan-2-one (18a).** From CuI (149 mg, 0.78 mmol), phenyllithium (1.1 mL of a 1.4 M solution, 1.5 mmol), and enone *E*-**4** (72 mg, 0.37 mmol) was obtained 34 mg (0.12 mmol, 33%) of **18a** as a white crystalline solid, mp 86−89 °C, $R_f$ 0.38 (10% EtOAc/hexanes), and 33 mg (0.11 mmol, 31%) of **18a** contaminated with traces of *E*-**4** after chromatography on silica gel 60 (70−230 mesh) eluted with 4% EtOAc/hexanes. Spectral data appear in the Supporting Information.

**(1*S*,4*R*,15*S*)-4-Methylbicyclo[13.1.0]hexadecan-2-one (19a) and (1*S*,4*S*,15*S*)-4-Methylbicyclo[13.1.0]hexadecan-2-one (19b).** From CuI (202 mg, 1.1 mmol), methyllithium (5.0 mL of a 0.4 M solution, 2.0 mmol), and enone *E*-**5** (103 mg, 0.44 mmol) were obtained 66 mg (0.26 mmol, 60%) of **19a**, $R_f$ 0.43 (10% EtOAc/hexanes), mp 59−61 °C, and 43 mg (0.17 mmol, 39%) of **19b**, $R_f$ 0.50, mp 51−53 °C, after chromatography on silica gel 60 (70−230 mesh) eluted with 3% $Et_2O$/hexanes. Spectral data appear in the Supporting Information.

**(*R*)-3-Methylcyclononanone (20) and (3*R*,7*R*)-3,7-Dimethylcyclooctanone (21).** To a solution of Li (11 mg, 1.5 mmol) in $NH_3$ (1 mL) at −78 °C was added a solution of ketone **15a** (37 mg, 0.24 mmol) and *t*-BuOH (36 mg, 0.49 mmol) in ether (1 mL) via cannula. After 45 min, solid $NH_4Cl$ (150 mg, 2.8 mmol) and ether (10 mL) were added, and the reaction mixture was allowed to attain room temperature. The resulting solution was dried ($MgSO_4$) and filtered, and volatiles were removed. The residue (41 mg) was dissolved in $CH_2Cl_2$ (1 mL), and pyridinium dichromate (91 mg, 0.24 mmol) was added. After being stirred at room temperature for 12 h, the reaction mixture was filtered through a plug of silica gel eluted with ether. Volatiles were removed, and the residual oil was chromatographed on silica gel 60 (70−230 mesh, 25 g) eluted with 5% $Et_2O$/pentane to give 27 mg (0.18 mmol, 72%) of **20**, $R_f$ 0.30 (10% EtOAc/hexanes), as a colorless oil contaminated with <5% of **21**.

**Spectral data for 20:** $^1$H NMR $\delta$ 1.00 (3, d, $J$ = 6.5 Hz), 1.23−1.66 (8, m), 1.78−1.89 (2, m), 2.27 (2, ddm, $J$ = 13.2, 2.4 Hz), 2.35−2.49 (3, m); $^{13}$C NMR $\delta$ 23.4, 24.1, 24.4, 26.2, 26.3, 31.0, 35.6, 43.6, 51.8, 217.3.

**(*R*)-3-Methylcyclotridecanone (22a) and (3*R*,11*R*)-3,-11-Dimethylcyclododecanone (23).** From Li (28 mg, 4.0 mmol), ketone **17a** (89 mg, 0.43 mmol), and *t*-BuOH (63 mg,

(21) The author has deposited atomic coordinates for **16a** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

0.85 mmol) was obtained 81 mg of a colorless oil, $R_f$ 0.44 (10% EtOAc/hexanes), after oxidation with PDC (320 mg, 0.85 mmol) and chromatography on silica gel 60 (70−230 mesh, 30 g) eluted with 3% $Et_2O$/pentane. This material was shown by $^1H$ NMR to be a mixture of ca. 31 mg (0.15 mmol, 35%) of **22a** and ca. 50 mg (0.24 mmol, 56%) of **23**. Purification of **23** was accomplished by formation of the 2,4-dinitrophenylhydrazone derivative, which was recrystallized from hot 60% absolute ethanol/EtOAc. Cleavage of the DNP using catalytic $H_2SO_4$ in the presence of formaldehyde gave **23** as pale yellow crystals.

**Spectral data for 23:** $[\alpha]^{23}_D$ −40.1 (*c* 1.39, $CHCl_3$); IR (neat) $cm^{-1}$ 1695; $^1H$ NMR $\delta$ 0.95 (6, t, $J$ = 6.9 Hz), 1.15−1.44 (14, m), 2.12−2.30 (4, m), 2.48 (2, dd, $J$ = 11.5, 3.9 Hz); $^{13}C$ NMR $\delta$ 20.2, 21.0, 22.5, 24.3, 27.3, 30.8, 48.7, 211.6.

**(*S*)-3-Methylcyclotridecanone (22b) and (3*S*,11*R*)-3,11-Dimethylcyclododecanone (24).** From Li (8 mg, 1.2 mmol), ketone **17b** (21 mg, 0.10 mmol), and *t*-BuOH (15 mg, 0.20 mmol) were obtained 7 mg (0.03 mmol, 33%) of **22b**, $R_f$ 0.43, as a colorless oil and 8 mg (0.04 mmol, 40%) of **24**, $R_f$ 0.49 (10% EtOAc/hexanes), mp 34−37 °C, after oxidation with PDC (75 mg, 0.2 mmol) and chromatography on silica gel 60 (70−230 mesh, 25 g) eluted with 3% $Et_2O$/pentane. Spectral data appear in the Supporting Information.

**(3*R*,14*R*)-3,14-Dimethylcyclopentadecanone (26).** From Li (14 mg, 2.1 mmol), ketone **19a** (62 mg, 0.25 mmol), and *t*-BuOH (19 mg, 0.25 mmol) was obtained 23 mg (0.09 mmol, 37%) of **26**, $R_f$ 0.53 (10% EtOAc/hexanes), as a colorless oil after oxidation with PDC (187 mg, 0.50 mmol) and chromatography on silica gel 60 (70−230 mesh, 20 g) eluted with 3% $Et_2O$/pentane. Spectral data appear in the Supporting Information.

**(*S*)-3-Methylcyclohexadecanone (25b) and (3*R*,14*S*)-3,14-Dimethylcyclopentadecanone (27).** From Li (11 mg, 1.6 mmol), ketone **19b** (43 mg, 0.17 mmol), and *t*-BuOH (25 mg, 0.34 mmol) was obtained 20 mg of a colorless solid, $R_f$ 0.53 (10% EtOAc/hexanes), after oxidation with PDC (195 mg, 0.52 mmol) and chromatography on silica gel 60 (70−230 mesh, 20 g) eluted with 1.5% $Et_2O$/pentane. This material was shown by $^1H$ NMR to be a mixture of ca. 4 mg (0.016 mmol, 9%) of 3-methylcyclohexadecanone **25b** and ca. 16 mg (0.10 mmol, 46%) of **27**. Spectral data appear in the Supporting Information.

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**Supporting Information Available:** Spectral data for compounds *Z*-**4**, *E*-**4**, *E*-**5**, **7a**, **8a**, **14a**, **14b**, **16a**, **17a**, **17b**, **18a**, **19a**, **19b**, **22b**, **24**, **26**, and **27**, mass spectral fragment lists for compounds *Z*-**3**, **6a**, **12a**, and **13a**, $^1H$ and $^{13}C$ NMR spectra of new compounds, and an ORTEP structure for **16a** (56 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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