ratio was 8.2:1.0 on the basis of these integral ratios.

2-Azido-3-methyl-1-phenyl-1-butenyl Acetate (3h). This enol acetate **3h** was obtained as a single geometrical isomer, which was supported by ^{1}H NMR and ^{13}C NMR spectra: ^{13}C NMR ($CDCl_3$) δ 169.298, 136.982, 134.760, 133.630, 128.844, 128.716, 128.466, 100.400, 28.943, 20.338. The appearance of only 10 lines is compatible with the assigned single isomer.

Syntheses of Oxazoles 5 by Intramolecular Aza-Wittig Reaction of 3. General Procedure. To a stirred solution of β-(acyloxy)vinyl azide **3** (1.00 mmol) in dry cyclohexane (5.0 mL) in a sealed tube was added triethyl phosphite (or other phosphorus(III) reagents) (10.0 mmol). Nitrogen gas evolution started immediately and ceased after 1 h. The mixture was heated at 90 °C for 24 h with continued stirring. The cooled mixture was chromatographed on a short silica gel column, eluting with ethyl acetate–hexane (1:4), to give oxazoles **5**. These products were further purified on a preparative TLC (silica gel, ethyl acetate–hexane 1:4), depending on the purity.

2-Methyl-5-phenyloxazole (5a). To a stirred solution of 2-azido-1-phenylvinyl acetate (**3a**) (150 mg, 0.740 mmol) in dry cyclohexane (4.0 mL) in a sealed tube was added triethyl phosphite (1.23 g, 7.40 mmol). After being stirred at room temperature for 1 h, the colorless mixture was heated at 90 °C for 24 h with continued stirring. The cooled mixture was chromatographed on a silica gel column, eluting with ethyl acetate–hexane (1:4), to give 102 mg (86.8%) of **5a** as white solid: mp 55–57 °C (lit.[16a,b]); IR (CH_2Cl_2) 1590, 1570 cm^{-1}; NMR δ 7.71–7.29 (m, 5 H), 7.19 (s, 1 H), 2.52 (s, 3 H). Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.38; H, 5.96; N, 8.61.

Supplementary Material Available: Tables of IR, NMR, and microanalyses data for compounds **2**, **3**, and **5** (5 pages). Ordering information is given on any current masthead page.

(16) (a) Gabriel, S. *Chem. Ber.* **1910**, *43*, 1283. (b) Ibata, T.; Ryohei, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3597. (c) Houwing, H. A.; Wildeman, J.; van Leusen, A. M. *Tetrahedron Lett.* **1976**, 143. (d) Sych, E. P.; Belaya, L. P.; Umanskaya, L. P.; Smaznaya-Il'ina, E. D. *Ukr. Khim. Zh.* **1966**, *32*, 274; *Chem. Abstr.* **1966**, *65*, 2380a. (e) Bhatt, M. V.; Reddy, G. S. *Tetrahedron Lett.* **1980**, *21*, 2359.

Intramolecular Diels–Alder Reaction of α,β-Unsaturated Ester Dienophiles with Cyclopentadiene and the Dependence on Tether Length

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Cyclopentadiene compounds, tethered to an α,β-unsaturated ester functionality, have been prepared by the direct alkylation of the corresponding iodide or tosylate with cyclopentadienylmagnesium chloride. For example, tso-$CH_2CH_2C(CH_3)_2CH{=}CHCO_2C(CH_3)_3$ reacted with cyclopentadienylmagnesium chloride at 0 °C to yield the alkylated cyclopentadiene, which on heating at 75 °C underwent a Diels–Alder reaction to give an 81% yield of 4,4-dimethyltricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylic acid, *tert*-butyl ester. Isomerization of cyclopentadiene isomers, common with lithium and sodium carbanions, is not displayed with the Grignard reagent. Several functionalized cyclopentadienes have been prepared which differ in tether length. These substrates readily undergo intramolecular [4 + 2] cycloaddition at mild temperatures to produce tricyclic ring systems. The cycloaddition will proceed at even lower temperatures if catalyzed by diethylaluminum chloride. Pathways of cycloaddition favor incorporation of the tether linkage into a five- or six-membered ring.

Introduction

The predictability and selectivity with which the Diels–Alder reaction forms two bonds and four potential asymmetric centers has led to its wide-spread use in synthesis. The intermolecular Diels–Alder reaction has been particularly useful in natural product synthesis, since this reaction has the additional advantages of forming an extra ring, increased reactivity due to entropic factors, and additional regiochemical constraints yielding a marked increase in stereoselectivity and diastereoselectivity.

Cyclopentadiene has been used extensively for the formation of bicyclo[2.2.1]heptane compounds as precursors to natural products.[1c] The occurrence of these naturally occurring bridging sesquiterpenes has led to the development and use of the intramolecular cycloaddition with cyclopentadiene. Subsequent ring expansion of the resulting cycloaddition products has been employed in the total synthesis of several cedrane derivatives, cedrene,[2] cedrol,[2] and cedranediol.[3] The synthesis of sativene has also been achieved through ring expansion of an intramolecular Diels–Alder product.[4] Other examples include the current development of this methodology as an approach to the synthesis of sinularene, longifolene, as well as an alternate route to sativene.[5] Cleavage of the strained olefin, followed by further functional group modification has led to the recent synthesis of two naturally occurring triquinanes,[6] such as siliphinene[7] and capnellene.[8] Recent advances in asymmetric induction of the Diels–Alder reaction[10,11] have made this cycloaddition a promising me-

(1) For recent reviews on the intramolecular Diels–Alder reaction, see: (a) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. (b) Ciganek, E. *Org. React.* **1984**, *32*, 1. (c) Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183.

(2) (a) Breitholle, E. G.; Fallis, A. G. *Ibid.* **1976**, *54*, 1991. (b) Breitholle, E. G.; Fallis, A. G. *J. Org. Chem.* **1978**, *43*, 1964.

(3) Landry, D. W. *Tetrahedron* **1983**, *39*, 2761.

(4) (a) Snowden, R. L. *Tetrahedron Lett.* **1981**, *22*, 97. (b) Snowden, R. L. *Ibid.* **1981**, *22*, 101.

(5) (a) Attah-Poku, S. K.; Gallacher, G.; Ng, A. S.; Taylor, L. E. B.; Alward, S. J.; Fallis, A. G. *Tetrahedron Lett.* **1983**, *24*, 677. (b) Attah-Poku, S. K.; Alward, S. J.; Fallis, A. G. *Ibid* **1983**, *24*, 681. (c) Gallacher, G.; Ng, A. S.; Attah-Poku, S. K.; Antczak, K.; Alward, S. J.; Kingston, J. F.; Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 1709. (d) Attah-Poku, S. K.; Antczak, K.; Alward, S. J.; Fallis, A. G. *Ibid.* **1984**, *62*, 1717.

(6) For a review of polyquinanes, naturally occurring or of general synthetic interest, see: Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1.

(7) Sternbach, D. D.; Hughes, J. W.; Burdi, D. F.; Banks, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 2149.

(8) (a) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 855. (b) Sternbach, D. D.; Hughes, J. W.; Burdi, D. F.; Forstot, R. M. *Tetrahedron Lett.* **1983**, *24*, 3295. (c) Sternbach, D. D., unpublished results.

(9) An alternate route to capnellene is also in progress: Hellou, J.; Kingston, J. F.; Fallis, A. G., unpublished results.

0022-3263/89/1954-0434$01.50/0

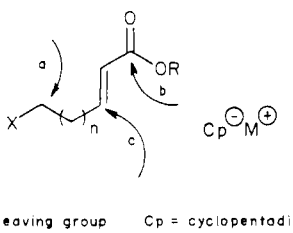


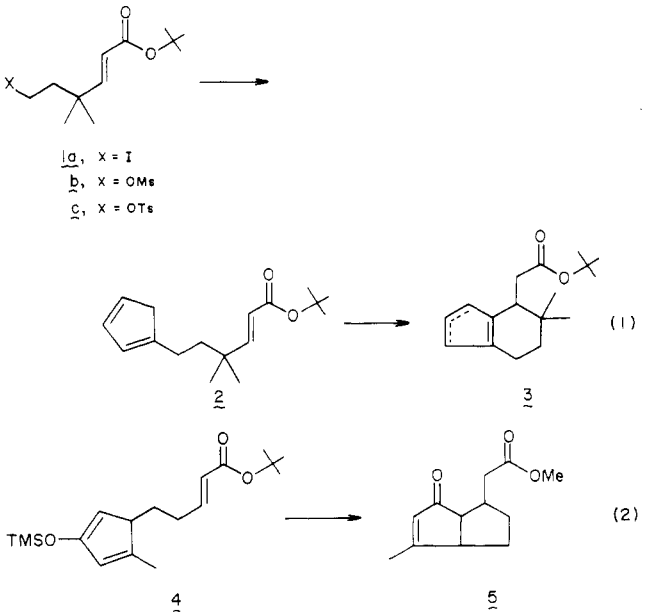
Figure 1. Modes of anion attack on substrate.

thod for the synthesis of optically active natural products.

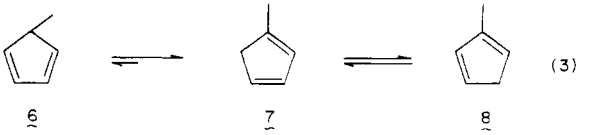
Intramolecular cycloadditions of cyclopentadiene containing α,β-unsaturated carbonyl dienophiles have been reported, but the examples are limited due to the general inaccessibility of these cyclopentadiene compounds. The routes used to prepare the reported substrates have involved specific diene formation or required elaborate synthetic construction. In the synthesis of cedranediol, the cyclopentadiene was cleverly masked as a dicyclopentadienyl moiety.[3] Unfortunately, the cedranediol synthesis was lengthy, and "deprotection" of the cyclopentadiene required elevated temperature (180 °C). In the synthesis of sativene[4] an alternate method was used: the in situ generation of a specific trisubstituted cyclopentadiene unit. Excellent cycloaddition yields were obtained after reaction at 110 °C for 3 days. Recently, approaches toward the synthesis of sinularene and longifolene have used a "blocked" cyclopentadiene in the intramolecular cycloaddition with an α,β-unsaturated ester.[5] The reaction proceeded at temperatures around 180 °C within 6 h. In the presence of the Lewis acid catalyst $AlCl_3$, the cycloaddition occurred within 3 h at temperatures as low as 23 °C. Organo-zinc and organo-magnesium reagents have recently been used to open the cyclobutanone ring of a bromobicyclo[3.2.0]heptenone system, producing a monosubstituted cyclopentadiene.[12] Intramolecular cycloaddition of these systems proceeded at room temperature within 20 h. The mild conditions under which these reactions proceed and their enormous synthetic potential encouraged us to investigate a general method for the preparation of compounds containing both cyclopentadiene moiety and an α,β-unsaturated ester functional group.

Herein we describe studies directed toward the general preparation of these compounds. A survey of their cycloaddition reactions through the structural analysis of the tricyclic products was performed using two-dimensional ^1H–^1H correlated NMR and difference nuclear Overhauser enhancement experiments. Our approach to the synthesis of these molecules involved the selective reaction of cyclopentadienyl anions with bifunctional substrates (Figure 1). In addition to the desired coupling reaction (path a), both 1,2-addition (path b) and 1,4-addition (path c) to the α,β-unsaturated carbonyl were possible. The tendency for the leaving group to undergo displacement and the nature of the metal counterion were found to effect the selectivity of this reaction.

With the use of cyclopentadienyl sodium or lithium, the alkylated products undergo base-catalyzed isomerization instead of [1,5]-shifts.[13] Alkylation of **1a** or **1b** with cyclopentadienylsodium or -lithium resulted in the intramolecular conjugate addition of the proposed intermediate **2** to the two olefinic isomers **3** (eq 1).[14] Similarly, the transformation of **4** and **5** has been reported (eq 2).[4a] The



alkylation of cyclopentadienylmagnesium bromide is somewhat different.[15] Methylation of this anion resulted in the initial formation of 5-methylcyclopentadiene (**6**, eq 3). After 4 h at room temperature, this isomer was almost completely converted to 1-methylcyclopentadiene (**7**). There is no evidence for the faster base-catalyzed isomerizations seen in the sodium and lithium salts. Isomerization of the methylcyclopentadienes continued, and, after 4 days at 25 °C, an equilibrium mixture of the three dienes had been reached. An equilibrium mixture of the dienes was also obtained by distillation (72.5 °C, 747 mm) of any one of the separate isomers. At equilibrium, the ratio of **7** to **8** was found to be approximately 0.8:1.0 with about 1% **6**. The compatibility of Grignard reagents with alkylcyclopentadienes has also been demonstrated in the preparation of the functionalized dienes previously discussed.[12]

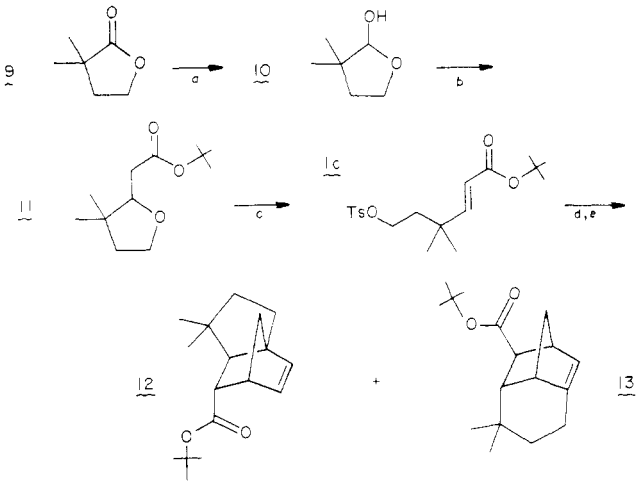


Results and Discussion

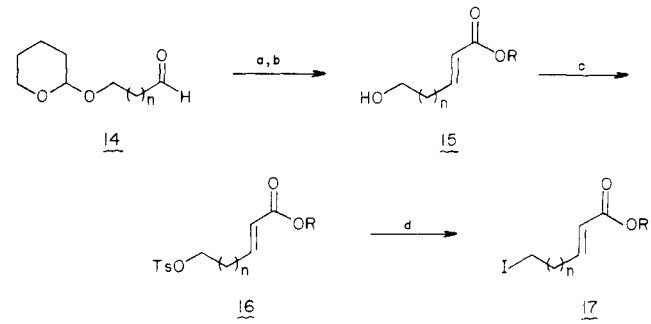
Initial investigations were conducted with **1c**, a substrate similar to that known to undergo deprotonation and intramolecular Michael addition to form **3** (eq 1).[14] The geminal dimethyl group was expected to reduce the possibility of the 1,4-addition to the α,β-unsaturated ester due to the steric hindrance and allowed the use of the tosylate as a leaving group. Also **1c** led to a precursor in the synthesis of the marine sesquiterpene capnellene.[8a] For the purposes of synthetic application, the existing synthesis of the alcohol precursor to this 4,4-dimethyl substrate was too lengthy.[16]

(10) For a review on asymmetric Diels–Alder reactions, see: Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876.
(11) (a) Evans, D. A.; Chapman, K. T.; Bisaha, J. *Tetrahedron Lett.* **1984**, *25*, 4071. (b) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1984**, *106*, 4261. (c) Oppolzer, W.; Chapuis, C.; Kelly, M. J. *Helv. Chim. Acta* **1983**, *66*, 2358. (d) Roush, W. R.; Gillis, H. R. Ko, A. I. *J. Am. Chem. Soc.* **1982**, *104*, 2269. (e) Ensley, H. E.; Parnell, C. A.; Corey, E. J. *J. Org. Chem.* **1978**, *43*, 1610.
(12) Wallquist, O.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1983**, *66*, 1891.
(13) McLean, S.; Haynes, P. *Tetrahedron* **1965**, *21*, 2329.
(14) Sternbach, D. D.; Hughes, J. W.; Burdi, D. F. *J. Org. Chem.* **1984**, *49*, 201, and unpublished results.
(15) Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. *Tetrahedron* **1963**, *19*, 1939.

Scheme I

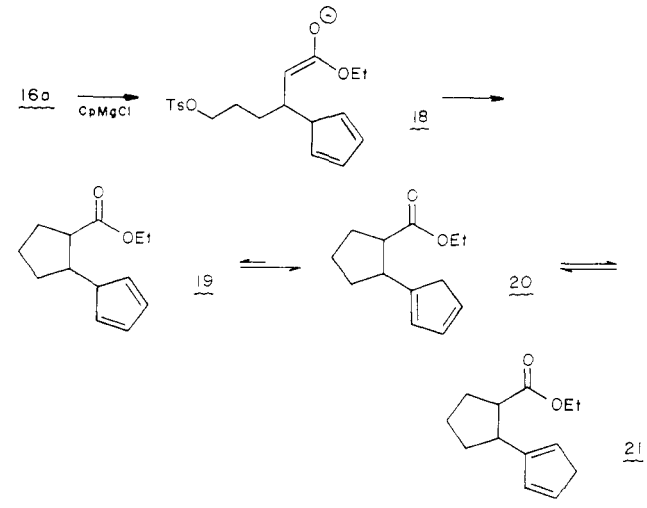


Scheme II[a]



[a] (a) R = Et, n = 2; (b) R = tBu, n = 2; (c) R = tBu, n = 3; (d) R = tBu, n = 1.

Scheme III



Instead, **1c** was prepared as shown in Scheme I. Reduction of α,α-dimethyl-γ-butyrolactone (**9**)[17] with diisobutylaluminum hydride produced a solution of the corresponding lactol (**10**).[18,19] Condensation of the lactol with the anion of $(EtO)_2POCH_2CO_2(CH_3)_3$ proceeded rapidly; however, under the basic conditions of the reaction, intramolecular Michael addition of the hydroxyl group to produce the tetrahydrofuran adduct **11** in 89% isolated yield also occurred. Treatment of this product with lithium diisopropylamide, followed by the addition of *p*-toluenesulfonyl chloride, furnished the desired crystalline tosylate **1c** in 83% yield. The coupling reaction of **1c** with cyclopentadienylmagnesium chloride or bromide[20] produced optimal results with use of 2.0 equiv of the Grignard reagent. Use of excess cyclopentadienyl reagent reduced the reaction time and eliminated side products that results from insufficient amounts of a cyclopentadienyl source. Within 3 h at 0 °C, the reaction had consumed all starting tosylate. Analysis of the product mixture by 400-MHz ^{1}H NMR revealed the presence of monosubstituted cyclopentadienes and an α,β-unsaturated ester olefinic protons. Despite the use of a 2-fold excess of cyclopentadienylmagnesium reagent, products resulting from the base-catalyzed intramolecular conjugate addition reaction were not observed.

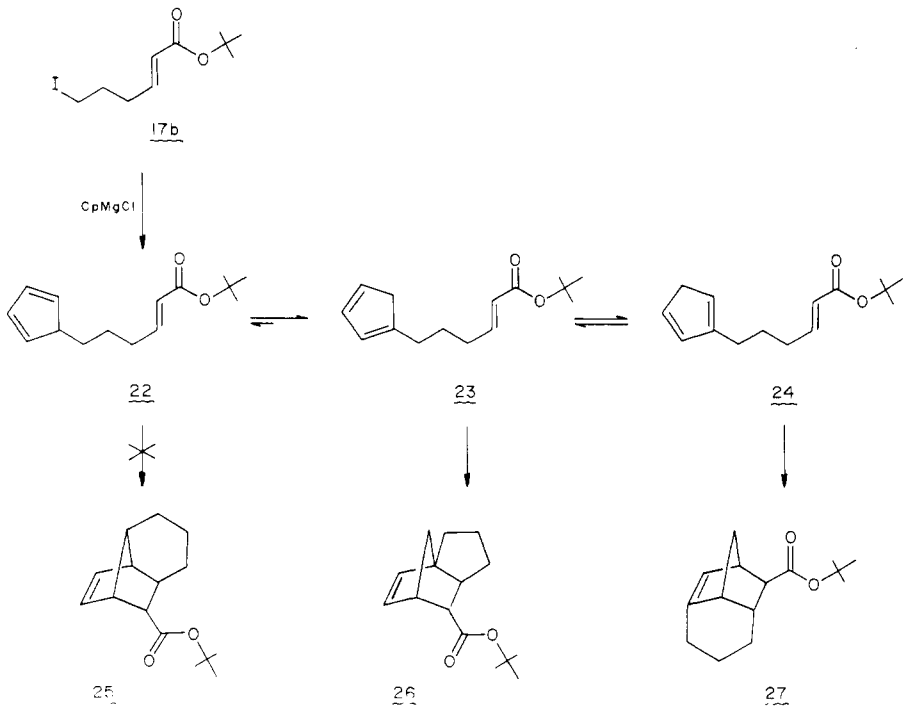
It was found that the intramolecular cycloaddition of **2** was dependent upon the temperature of the reaction mixture. When a benzene solution of **2** was heated in a 75 °C oil bath for 4 h, two cycloaddition products, **12** and **13**, were formed in a ratio of 91:9, respectively, as detected by capillary gas chromatography. At 100 °C, the ratio of **12** to **13** was 81:19. The major product was identified as **12** by the characteristic doublet at 6.21 ppm and the doublet of doublets at 5.99 ppm as observed by ^{1}H NMR.[21] Although not completely characterized, we suggest that the structure of the minor product was that of **13** due to spectral similarities with the tricyclic product **27**. The major product was isolated by allowing the 91:9 product mixture (which still contained traces of ether) to stand 24 h at ambient temperature during which time **13** completely disappeared and the amount of **12** remained constant. It is suspected that the strained, trisubstituted olefin **13** polymerized selectively, yielding nonvotile material from which the tricyclic adduct **12** was distilled in 81% yield. These results demonstrated that the Grignard reagent is a very promising route to functionalized cyclopentadienes.

To explore the application of CpMgCl in the general synthesis of functionalized cyclopentadienes, substrates with unsubstituted chains were prepared that differed in tether length, ester group, and leaving group. All substrates were readily prepared from the known, bifunctional tetrahydropyranoxy aldehydes (**14**).[22] Condensation with the appropriate phosphonate ester followed by deprotection of the hydroxy group, produced the crude alcohol **15** (Scheme II). Reaction with *p*-toluenesulfonyl chloride in pyridine transformed **15** into tosylate **16** with good overall yield. Conversion to the iodide **17** was achieved in excellent yield with NaI in acetone.

An attempt to use the tosylate salt **16a** in coupling reactions with cyclopentadiene Grignards proved unsuccessful. Although the tosylate reacted quickly, the products of the reaction (after refluxing in benzene) were not the expected cycloaddition products, but two monosubstituted α,β-saturated cyclopentadienes, identified by ^{1}H and ^{13}C NMR. An explanation for the disappearance of both the tosylate and the unsaturation in the substrate,

(16) Smith, A. B. III; Malamas, M. S. *J. Org. Chem.* **1982**, *47*, 3442.
(17) Baas, J. L.; Davies-Fidder, A.; Huisman, H. O. *Tetrahedron* **1966**, *22*, 285.
(18) Kraus, G. A.; Frazier, K. A.; Roth, B. D.; Taschner, M. J.; Neuenschwander, K. *J. Org. Chem.* **1981**, *46*, 2417.
(19) Castonguay, A.; Brassard, P. *Can. J. Chem.* **1977**, *55*, 1324.
(20) Both CpMgBr and CpMgCl are interchangeable in these reactions. However, CpMgCl is easier to prepare.
(21) For ^{1}H NMR information on bicyclo[2.2.1]heptene compounds, see: (a) Mellor, J. M; Webb, C. F. *J. Chem. Soc., Perkin Trans. 2*, **1974**, 26. (b) Davis, J. C., Jr.; Van Auken, T. *J. Am. Chem. Soc.* **1965**, *87*, 3900.
(22) (a) For n = 2: Vesato, S.; Kobayashi, K.; Inouye, H. *Chem. Pharm. Bull.* **1982**, *30*, 927. (b) For n = 3: Vig, O.P.; Sharma, M. L.; Gakhar, M.; Malik, N. *Ind. J. Chem. Sect. B* **1980**, *19*, 755. (c) For n = 1: Danieli, B.; Lesma, G.; Palmisano, G.; Tollari, S. *J. Chem. Soc., Perkin Trans. 1* **1984**, *1237*.

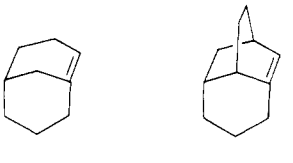
Scheme IV



despite the addition of only 1 equiv of CpMgCl, is shown in Scheme III. Initial conjugate addition of the cyclopentadienyl anion to **16a** resulted in the generation of enolate intermediate **18**[23] containing a β-chiral center (Scheme III). Rapid diastereoselective intramolecular alkylation by the tosylate would then produce a single 5-alkylcyclopentadiene **19**, which upon heating, isomerized to the two more stable substituted cyclopentadienes **20** and **21**. It is important to note that the intramolecular 1,4-addition process observed in eq 1 was not detected. The 1,2-addition to the carbonyl did not occur, and thus, the use of the corresponding *tert*-butyl ester **16b**, as expected, gave a similar product distribution upon reaction with CpMgCl. The *tert*-butyl esters were used in all subsequent reactions for reasons of spectroscopic convenience.

In order to enhance the desired coupling reaction in preference to the conjugate addition, a better leaving group was employed. Reaction of CpMgCl with the iodide **17b** produced much more favorable results. At 0 °C, the coupling of **17b** with CpMgCl was complete within an hour. Following removal of the magnesium salts, a benzene solution of the mixture was maintained at reflux for 2 h until cycloaddition was complete. Analysis of the solution revealed that only 14% of the mixture was due to the unwanted intermolecular Michael addition side products analogous to **20** and **21**. The balance of the mixture was composed of two cycloaddition products that were present in a ratio of 6.4:1.0. The conjugate addition side products were readily separated from the mixture by selective reaction with maleic anhydride and subsequent flash chromatography. The major isomer **26** (Scheme IV) was identified as the unsubstituted analogue of **12** through its characteristic ^{1}H NMR olefinic resonances. The doublet at 6.20 ppm and the doublet of doublets at 5.91 ppm confirmed the presence of a bridgehead substituent and, thus, the topology of the tricyclic structure **26**. This product was a result of the intramolecular cycloaddition of the 1-substituted cyclopentadiene **23**.

The presence of minor amounts of a second isomer was unanticipated. Previous examples of intramolecular cycloaddition of olefins to cyclopentadiene, separated by a three-carbon tether, had always produced a single product.[1,2,8b] ^{1}H NMR spectra verified the presence of a bicyclo[2.2.1]hept-2-ene ring skeleton contained within the resulting tricyclic structure. In contrast to **12**, there were two distinctive bridgehead proton signals at 3.00 and 2.59 ppm and only one olefinic proton resonance (5.55 ppm). The carbon spectrum of this product revealed two olefinic carbons, one of which had a proton substituent. ^{1}H NMR and ^{13}C NMR spectral data suggested a tricylic skeleton with the structure **27**.[21] This product was formed through the cycloaddition of the 2-substituted cyclopentadiene **24**. The intramolecular cycloaddition of **24** to form a bridgehead olefin was not expected.[2a] To our knowledge this type of skeletal structure has not been previously reported; however, similar bridgehead olefin compounds have been prepared. The unsubstituted analogue, lacking the bridge methylene carbon, bicyclo[3.3.1]non-1-ene (**28**), has been prepared by several independent methods.[24] Another similar compound that contained a bridgehead olefin resulted from the intramolecular Diels–Alder reaction involving a 2-substituted cyclohexadiene in the formation of **29**.[25] However, neither of these examples contained the additional conformational strain that is inherent in a bicyclo[2.2.1]hept-2-ene skeleton.



(23) For examples of magnesium enolates generated by conjugate addition to α,β-unsaturated carbonyls, see: (a) Mukaiyama, T.; Iwasawa, N. *Chem. Lett.* **1981**, 913. (b) Munch-Peterson, J. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 762.

(24) (a) Nakazaki, M.; Naemura, K.; Nakahara, S. *J. Chem. Soc., Chem. Commun.* **1979**, 82. (b) Shea, K. J.; Wise, S.; Burke, L. D.; Davis, P. D.; Gilman, J. W.; Greeley, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 5708.

(25) Bridges, A. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1975**, *2264*.

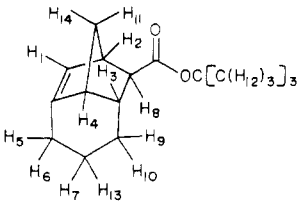


Figure 2. Proton assignments of 27.

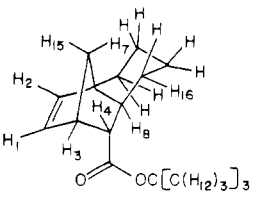
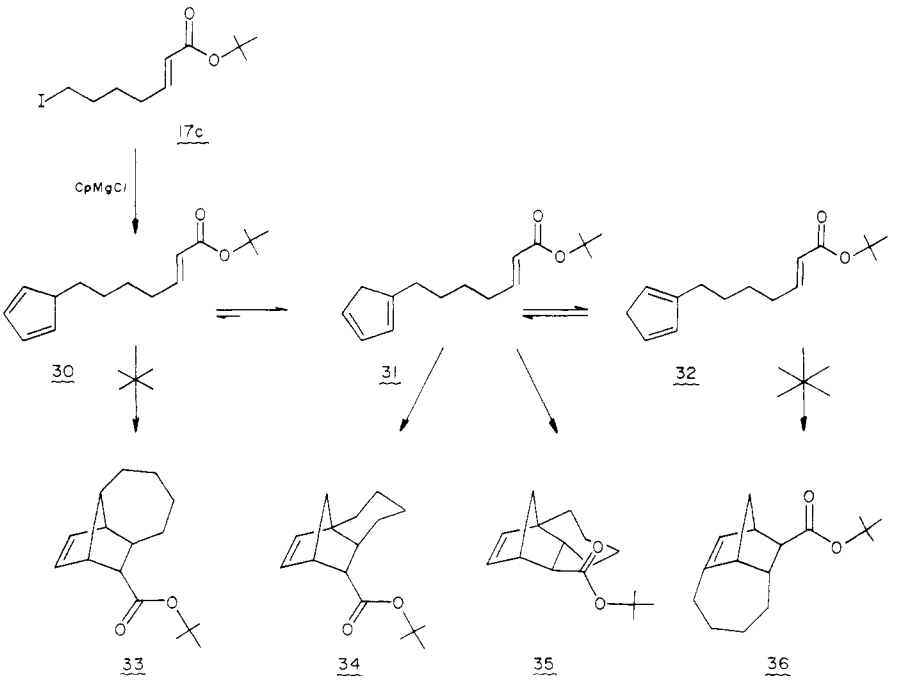


Figure 3. Proton assignments of 34.

Scheme V



The structure of **27** was determined through the use of ^1H–^1H correlated two-dimensional NMR[26] and difference nuclear Overhauser enhancement (NOE) experiments. The crosspeaks that occurred off the diagonal in ^1H–^1H correlated two-dimentional NMR, as a result of J coupling between two protons, were used to trace the carbon framework of the molecule. From the strong coupling of proton H_1 (5.55 ppm) to that of the bridgehead proton at 3.00 ppm, proton H_2 was identified (Figure 2). Proton H_2 displayed strong coupling to both bridge protons H_{11} and H_{14}, which, in turn showed coupling to the other bridgehead proton H_4. Coupling between protons H_2 and H_8 or H_4 and H_3 were not observed. In spite of the absence of coupling, the regiochemistry of the cycloaddition was assumed due to the constraints imposed by the three-carbon tether. Further assignment of proton chemical shifts were made by tracing the coupling of H_8 to H_3, which also displayed J coupling to H_9 and H_{10}. The overlapping protons H_9 and H_{10} couple to both H_7 and H_{13}, which also coupled to one another. Protons H_7 and H_{13} each coupled to the two allylic proton resonances H_5 and H_6, which are also generally coupled. Due to the pulse delays chosen for this experiment, weak four-bond coupling between H_1 and H_{11}, and that of proton H_2 and H_4, were observed by the occurrence of crosspeaks. The structure of **27** was verified through the use of ^1H–^1H correlated two-dimensional NMR.

Further information on the regiochemistry that resulted from the cycloaddition was obtained through difference nuclear Overhauser enhancement (NOE) studies. Saturation of proton H_1 resulted in the enhancement of proton H_2, H_5, and, to a lesser degree, H_8. Proton H_2, upon saturation displayed similar enhancement of H_1 and enhancement of H_8. As expected, protons H_1 and H_2 were enhanced upon saturation of H_8. Because H_7 overlapped slightly with H_8, the partial saturation of H_7 occurred, producing enhancement of H_{13}. Although the resonance of H_3 and H_4 were too close to show relative interaction between the two protons, saturation of H_3 did result in the enhancement of both H_8 and H_{11}; the slight enhancement of H_9 and H_{10} were also observed. These experiments verified the regiochemistry of the $4\pi + 2\pi$ cycloaddition and demonstrated ester functionality to be an exo substituent.

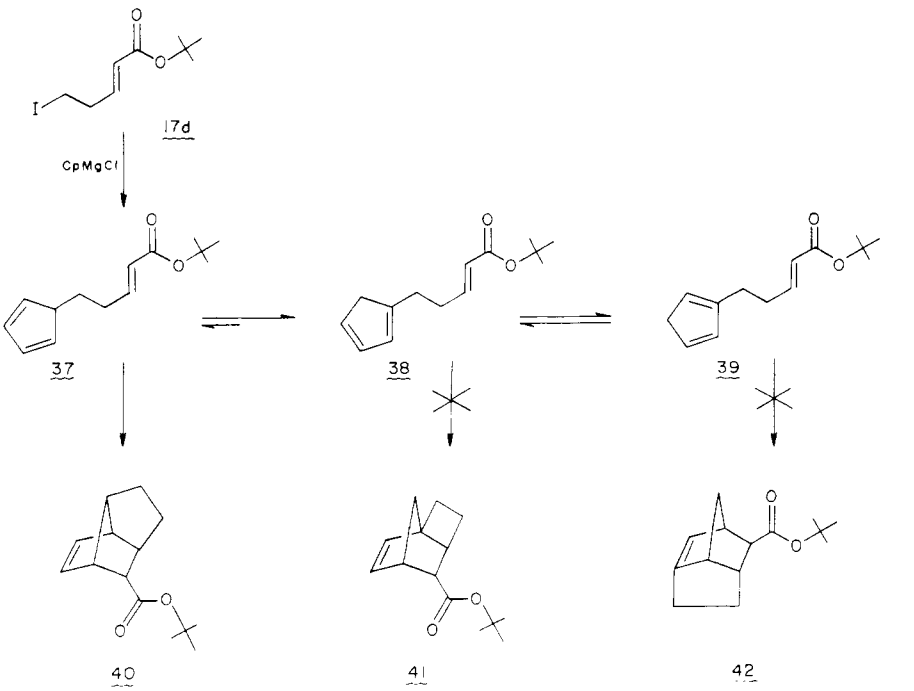
As expected, product selectivity in the cycloaddition reaction was enhanced at lower temperature. At room temperature (5-day period), the products **26** and **27** were formed in a 98.5:1.5 ratio. At −15 °C, the cycloaddition reaction catalyzed by 1.4 equiv of Et_2AlCl produced only **26** as observed by capillary gas chromatography.

With the four-carbon tether, four possible cycloaddition products can arise (Scheme V). The reaction of **17c** with 1.00 equiv of CpMgCl produced the substituted cyclopentadiene **30**. The mixture was heated to reflux in benzene until cycloaddition was complete (4 h). Analysis of the mixture revealed that intramolecular conjugate addition to the α,β-unsaturated ester had occurred to an extent of only 9%. Two cycloaddition products, in a ratio of 69:31, initially detected by capillary gas chromatography were isolated by flash chromatography.

The major isomer **34** was obtained in 40% isolated yield, and the structure was elucidated by NMR spectroscopy.

(26) For information on two-dimensional NMR, see: Bax, A. *Two-Dimensional Nuclear Magnetic Resonance in Liquids*; Reidel: Boston, 1982.

Scheme VI



An olefinic resonance at 5.99 ppm appeared as a doublet of doublets; that at 5.85 ppm was a doublet. This coupling pattern indicated that the product was the result of the cycloaddition of the 1-substituted cyclopentadiene **31**. In overall appearance, the proton spectrum was quite similar to that of **26**. Two-dimensional ^1H–^1H correlated NMR revealed the positions of all the protons not present in the tether (Figure 3). The olefin doublet (proton H_2) displayed coupling to the other olefin resonance (H_1), which showed coupling to the bridgehead proton H_3. Proton H_3 coupled to both H_7 and H_{15} on the methylene bridge, as well as to the α-carbonyl proton H_4. Proton H_8 was assigned as a result of the crosspeak resulting from J coupling to H_4. Due to resonance overlap, assignment of individual tether protons could not be made. The use of two-dimensional ^1H NMR allowed the skeletal connectivity and assignments of individual protons to be made but could not distinguish between isomers **34** and **35**; difference NOE studies accomplished this.

The minor product **35** was isolated in a 17% yield and was also identified by NMR spectroscopy. The proton NMR spectrum of this compound similarly exhibited the pattern of olefinic protons at 6.23 and 6.01 ppm resulting from the cycloaddition of **31**. A single bridgehead proton was also observed at 2.79 ppm. The NMR spectrum of **35** showed very few other similarities to that of **34**. There were no other proton resonances observed downfield of 2.00 ppm. The many overlapping protons between 1.20 and 1.80 ppm greatly hindered characterization of **35**.

Two-dimensional ^1H–^1H correlated NMR aided in the partial assignment of proton resonances of **35** (Figure 4). From the two dimensional spectrum, it was easily seen that the J coupling between proton H_2 and H_1 was very strong. Proton H_2 also displayed strong coupling to the bridgehead proton H_3, which, in turn, showed crosspeaks resulting from the coupling with the bridge protons H_6 and H_7. The distinctive pattern of the bridge protons could be distinguished among the other protons. As was the case for the exo substituted ester **27**, coupling between H_3 and H_5 was not detected in the ^1H–^1H correlated spectrum. Through the use of difference NOE experiments, the distinction between exo and endo substitution was made. Saturation

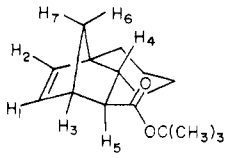


Figure 4. Proton assignments of **35**.

of H_1 showed enhancement of proton H_2 and H_3 as expected but also enhanced a third proton previously believed to be H_5. Saturation of proton H_4 produced enhancement of the proton known to be H_6 and that suspected of being H_5. The results obtained from these experiments verified the exo position of the ester substituent and, thus, the confirmation of **35** as the minor isomer.

In order to increase selectivity in the cycloaddition of **31**, a solution of **31** and Et_2AlCl in CH_2Cl_2 was allowed to react at −15 °C for 12 h. Analysis of the product distribution by capillary gas chromatography revealed a 73:27 ratio of **34** to **35** as the only cycloaddition products. Very little increase in product selectivity was exhibited under these conditions as compared to the product distribution obtained in refluxing benzene.

On the basis of previously reported examples, the shorter tether of only two methylene units was expected to give a single product.[1] Via the normal procedure, a solution of 1.00 equiv of CpMgCl was added to a solution of the iodide **17d** and stirred for 1 h at 0 °C. A toluene solution of the product mixture was heated to reflux and maintained at that temperature for 18 h. These conditions produced a single cycloaddition product that was to 78% of the reaction mixture, while the remaining product (22%) was the result of an intermolecular Michael addition. Isolation of the cycloaddition product was achieved in 53% yield.

Through the use of ^1H NMR, the structure of the product **40** (Figure 5) was determined (Scheme VI). As expected from previous work on intramolecular Diels–Alder reactions with the cyclopentadienes, two patterns became evident. Products tended not to form as a result of 5-substituted cyclopentadiene intermediate. The products formed also had exclusive preference for five- and

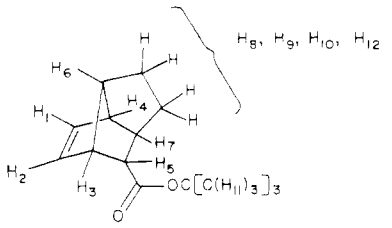


Figure 5. Proton assignments of **40**.

six-membered ring formation. From the coupling of **17b** with cyclopentadiene, the tricyclic structures did not arise from **23** even though the tether would have formed a six-membered ring. Instead, the tether became a part of a five-membered ring as in product **26** and a six-membered ring in **27**. Tricyclic structures that resulted from a four-carbon tether, as in the alkylation of **17c**, produced only **34** and **35**. This demonstrated the preference for the six-membered over the seven-membered ring systems of both **33** and **36**. If a stable five- or six-membered ring system could not be formed by any other intramolecular cycloaddition, it could occur from the 5-substituted cyclopentadiene such as **37**. The formation of **42** was unfavorable due to the generation of a structurally disallowed bridgehead olefin. Due to the added strain of a cyclobutane ring, **41** was not observed. However, for the formation of **40** required elevated temperatures and longer reaction times.

The use of CpMgCl in the preparation of functionalized cyclopentadienes has already proven valuable as a method to prepare molecules of synthetic and theoretical interest. Compound **12** served as a key intermediate in the efficient synthesis of capnellene.[8a] This synthetic strategy shows considerable potential for the synthesis of many other polyquinanes.[6] The greater reactivity of the dienophile has also allowed the unexpected formation[2a] and subsequent isolation of the tricyclic bridgehead olefin **27**. The selective formation of functionalized cyclopentadienes through the use of cyclopentadienyl Grignard reagents, by intramolecular cycloaddition under mild conditions, provides an attractive route to naturally occurring ring systems.

Experimental Section

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out with use of standard Schlenk or vacuum line techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves. Solids were transferred in a nitrogen-filled Vacuum Atmospheres Dri-Lab equipped with an MO-4-1 purification train and a DK-3E Dri-Kool. Flash chromatography was performed according to the general procedure of Still,[27] employing Silica Woelm 32-63 (32–63 μM). Analytical thin-layer chromatography (TLC) was performed with use of EM Reagents 0.25 mm silcia gel 60-F plates and visualized by phosphomolybdic acid dip.[28] All reaction temperatures were measured externally.

Materials. Diisopropylamine (Aldrich) was distilled from CaH_2 before use. Mesitylene (MCB Reagents) was stored over 4-Å molecular sieves under argon. Pyridinium *p*-toluenesulfonate,[29] $(EtO)_2POCH_2CO_2C(CH_3)_3$,[30] and **14**[22] were prepared by reported methods. With the exception of NaI (Mallinckrodt), Et_2AlCl (Alfa), hydroquinone (MCB Reagents), and *p*-toluenesulfonyl chloride (MCB Reagents), all other chemicals were obtained from the Aldrich Chemical Co. and used without further purification. $CDCl_3$ was stored over 4-Å molecular sieves and filtered through Activity I alumina immediately prior to use. Pyridine was stored over 4-Å molecular sieves. Dichloromethane was dried over P_2O_5 and degassed on a vacuum line. Pentane was stirred over H_2SO_4, dried over CaH_2, and vacuum transferred onto sodium benzophenone ketyl. Benzene and tetrahydrofuran (THF) were dried over CaH_2 and vacuum transferred onto sodium benzophenone ketyl. Diethyl ether (ether), toluene, benzene-d_6 (Cambridge Isotope Laboratories), and THF-d_8 (Cambridge Isotope Laboratories) were degassed and stirred over sodium benzophenone ketyl. The dried and degassed solvents were vacuum transferred into dry vessels equipped with Teflon valve closures and stored under argon. Reagent grade petroleum ether (35–60 °C) was used without further purification.

Instrumentation. NMR spectra were recorded on a JEOL GX-400 (399.65 MHz ^1H; 100.40 MHz ^{13}C). Chemical shifts are reported versus residual solvent signals on the δ scale. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad), coupling constant (hertz), integration, and interpretation. Difference NOE experiments were performed according to published procedures, and the results are described fully in the text of this paper.[31] Analytical gas chromatographic analysis (VPC) were performed on a Shimadzu GE-Mini 2 flame ionization instrument modified for capillary use and equipped with a Hewlett-Packard Model 399A integrator (column: 0.24 mm × 15 m DB1). The detector and injector temperature were 250 °C. Column temperature and retention times (t_R) are as reported. Infrared analyses utilized a Beckman 4210 spectrophotometer and are reported in reciprocal centimeters (cm^{-1}). Melting points were determined on a Thomas-Hoover Unimelt capillary melting point apparatus and were uncorrected.

Combustion analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN) or by Lawrence Henling at the California Institute of Technology Microanalytical Laboratory.

Two-Dimensional ^1H–^1H Correlated NMR Spectra.[26] The data were acquired with a JEOL GX-400 NMR spectrometer operating at 399.65-MHz proton frequency. The pulse sequence was 90°–t_1–45°–acquisition–relaxation delay; the phase of the pulses and receiver were cycled to provide quadrature detection in f_1 and selection of "P-type" peaks. The 90° ^1H pulse width on the 5 mm $^1H/^{13}C$ probe was 15.0 μs. The f_2 spectral width was 3201.0 Hz and the pulse delay (PD) was 3.0 s. Two dummy scans were taken before each slice to eliminate nonequilibrium magnetization. Eight transients of 1K data points were collected for 384 increments of t_1. The total acquisition time was 3.5 h. The data were zero-filled to 512 points in t_1, apodized with a sine-bell window function in both dimensions, and Fourier transformed in both dimensions. The absolute value spectrum was calculated, and the entire data set was symmetrized.

Cyclopentadienylmagnesium Bromide. A solution of 30 mL of MeMgBr (2.9 M, 87.0 mmol in ether) was concentrated in vacuo and redissolved in an equal volume of THF. To this solution was added 11.50 g of freshly distilled cyclopentadiene (174 mmol) at room temperature. The mixture was then heated to 75 °C over the period of 30 min and maintained at that temperature for 4 h. After the solution was allowed to cool to ambient temperature, the mixture was concentrated to a slushy solid and placed under vacuum (0.001 mmHg) for 1 h. The nonvolatiles were dissolved in a minimal amount of ether/THF (1:1) and filtered, and the mother liquor was allowed to cool to −25 °C. This process produced crystalline material, which the was washed with cold ether (3 × 40 mL) to produce 22.50 g of crystalline solid.

To quantify the amount of CpMgBr per weight of while solid, integration of the cyclopentadienyl singlet (δ 6.03) was compared to that of added mesitylene. To a solution of 40 mg of CpMgBr·*n*(THF) in 0.500 mL of THF-d_8 was added mesitylene (8.8 mg, 0.073 mmol). Integral comparison to the mesitylene methyl groups showed the presence of 0.106 mmol of CpMgBr. Thus, it was found that there were 377 mg of powder per millimole of CpMgBr and that the overall yield of isolated CpMgBr, based

(27) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43* 2923.
(28) Touchstone, J. C.; Dobbins, M. F. *Practice of Thin Layer Chromatography*; Wiley: New York, 1978; p 207.
(29) Miyashita, N.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.
(30) Griffiths, G. F.; Kenner, G. W.; McCombie, S. W.; Smith, K. M.; Sutton, M. J. *Tetrahedron* **1976**, *32*, 275.
(31) (a) Hall, L. D.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1980**, *102*, 5703. (b) Sanders, J. K.; Mersh, J. D. *Prog. Nucl. Magn. Reson. Spectrosc.* **1982**, *15*, 353.

on MeMgBr, was 59.6 mmol (69%).

Cyclopentadienylmagnesium Chloride. To 21.7 mL of 3.0 M MeMgCl (65.0 mmol in THF) under argon atmosphere was added freshly distilled cyclopentadiene (8.59 g, 130 mmol). This mixture was stirred for 2 h at room temperature after which 10 mL of THF were added. The reaction mixture was heated to 65 °C over the period of 30 min and maintained at that temperature for 2 h. After the solution was allowed to cool to ambient temperature, the mixture was concentrated to a slushy solid and placed under vacuum (0.001 mmHg) for 1 h. The mixture was washed (removal of liquid was performed via cannula) with ether (3 × 10 mL), pentane (2 × 15 mL), and once again with 10 mL of ether. Residual solvent was removed in vacuo to produce 9.72 g of CpMgCl·*n*(THF) as a white powder. As with CpMgBr, there were 378 mg of powder per millimole of CpMgCl, and the overall yield of isolated CpMgCl, based on MeMgCl, was 25.7 mmol (40%).

α,α-Dimethyl-γ-butyrolactone (9). A suspension of 40.83 g of oil-free NaH (1.70 mol) in 700 mL of dry THF was brought to reflux. To this vigorously stirred suspension was added a mixture of 270.5 g of CH_3I (1.91 mol) and 58.6 g of γ-butyrolactone (0.68 mol) over the period of 1.5 h. Reflux was then maintained for an additional 1.5 h. After the mixture was cooled to 0 °C, H_2O was added, and the mixture was then acidified with 1 N HCl. The aqueous mixture was continuously extracted with diethyl ether for 20 h. After removal of the solvent by distillation at atmospheric pressure, the product was distilled (bp 65 °C, 8 mmHg) (lit. 10 mmHg, 74 °C) to yield a slightly yellow oil. This oil was dissolved in ether and washed with saturated aqueous Na_2SO_3, and the aqueous layer was extracted twice with ether. The organics were combined, dried over $MgSO_4$, and evaporated to give 58.86 g (76%) of **9** as a colorless oil: ^{1}H NMR (400 MHz, CDC13) δ 4.20 (t, *J* = 7.0 Hz, 2 H, CH_2O), 2.06 (t, *J* = 7.0 Hz, 2 H, CH_2CH_2O), 1.20 (s, 6 H, CH_3); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 181.8, 64.7, 38.7, 37.1, 24.3.

2,2-Dimethyl-4-hydroxybutanal (10). A solution of 10.00 g of **9** (87.6 mmol) was dissolved in 200 of mL of dry, deoxygenated toluene under an argon atmosphere and cooled to −78 °C. A solution of 1.00 M diisobutylaluminum hydride (96.4 mmol in hexanes) was slowly added over the period of 15 min. The reaction mixture was stirred an additional 30 min at −78 °C and was then poured into a rapidly stirring mixture of 90 mL of acetic acid and 300 g of ice. To this mixture was added 640 mL of chloroform. After being stirred for 10 min, the aqueous layer was separated and extracted three times with chloroform. The organic layers were combined, washed twice with saturated aqueous $NaHCO_3$, and dried over Na_2SO_4. The solution was then concentrated at reduced pressure (20 mmHg) at or below 0 °C until it reached a volume of 225 mL. This solution of **10** was used without further purification.

(Tetrahydro-3,3-dimethyl-2-furanyl)acetic Acid, *tert*-Butyl Ester (11). A suspension of 2.31 g of oil-free NaH (96.4 mmol) in 50 mL of dry, deoxygenated benzene was cooled to 0 °C. To this suspension was added a solution of 24.31 g of $(EtO)_2POCH_2CO_2C(CH_3)_3$ in 30 mL of benzene over the period of 15 min. The reaction mixture was stirred for an additional 15 min at 0 °C, warmed to room temperature, and then stirred at ambient temperature for 30 min. The solution of **10** (≈87.6 mmol) was added slowly at such a rate so as not to exceed an internal reaction temperature of 35 °C. After the addition was complete, the mixture was stirred an addition 10 h at room temperature. The reaction mixture was then quenched with water and extracted three times with $CHCl_3$. The organics were washed with water, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl and then dried over $MgSO_4$. The organics were filtered through a pad of silica gel, washed with ether, and concentrated in vacuo. Distillation from MgO (Kugelrohr, 55–65 °C, 5 mmHg) yielded 16.73 g of **11** (89%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (ddd, *J* = 7.7, 8.4, 8.9 Hz, 1 H, OCH_2), 3.77 (ddd, *J* = 4.9, 8.4, 8.9 Hz, 1 H, OCH_2), 3.76 (t, *J* = 6.6 Hz, 1 H, OC*H*), 2.24 (d, *J* = 6.6 Hz, 2 H, $CH_2CO_2C(CH_3)_3$), 1.74 (ddd, *J* = 8.4, 8.4, 12.1 Hz, 1 H, OCH_2CH_2), 1.66 (ddd, *J* = 4.9, 7.7, 12.1 Hz, 1 H, OCH_2CH_2), 1.41 (s, 9 H, $C(CH_3)_3$), 1.01 (s, 3 H, CH_3), 0.86 (s, 3 H, CH_3); ^{1}H NMR (400 MHz, C_6D_6) δ 3.97 (dd, *J* = 3.8, 9.4 Hz, 1 H, OC*H*), 3.67 (ddd, *J* = 7.8, 8.2, 8.7 Hz, 1 H, OCH_2), 3.59 (ddd, *J* = 4.9, 8.5, 8.7 Hz, 1 H, OCH_2), 2.38 (dd, *J* = 9.4, 14.7 Hz, 1 H, $CH_2CO_2C(CH_3)_3$), 2.16 (dd, *J* = 3.8, 14.7 Hz, 1 H, $CH_2CO_2C(CH_3)_3$), 1.41 (s, 9 H, $C(CH_3)_3$), 1.35 (ddd, *J* = 8.2, 8.5, 12.2 Hz, 1 H, OCH_2CH_2), 1.27 (dd, *J* = 4.9, 7.8, 12.2 Hz, 1 H, OCH_2CH_2), 0.78 (s, 3 H, CH_3), 0.66 (s, 3 H, CH_3); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 170.7, 82.9, 80.4, 65.5, 41.0, 37.1, 28.3, 25.6, 22.0; IR (neat) 2965, 2880, 1734, 1370, 1315, 1150 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.26; H, 10.35. Found: C, 67.10; H, 10.19.

(*E*)-4,4-Dimethyl-6-[[(4-methylphenyl)sulfonyl]oxy]hex-2-enoic Acid, *tert*-Butyl Ester (1c). To a solution of 2.48 g of diisopropylamine (2.45 mmol) of 70 mL of dry, deoxygenated THF under argon at −78 °C, was added a solution of 1.60 M *n*-butyllithium (24.5 mmol in hexanes) via syringe. The mixture was allowed to react for 20 min at −78 °C, and then a solution of 4.78 g of **11** (22.3 mmol) in 10 mL of THF was slowly added. The reaction mixture was stirred at −78 °C for 15 min and then warmed to −40 °C. After being stirred at −40 °C for 20 min, the solution was returned to −78 °C at which time *p*-toluenesulfonyl chloride was added under a heavy flow of argon. The mixture was allowed to warm to room temperature slowly over the period of 8 h and to stir an additional 9 h at room temperature. After quenching with 200 mL of 1 N HCl, the mixture was extracted with ether (3 × 200 mL). The organics were combined, washed with 1 N HCl (1 × 200 mL), saturated aqueous $NaHCO_3$ (2 × 200 mL), and saturated aqueous NaCl, and dried over $MgSO_4$. The solution was concentrated to a yellow oil, taken up in petroleum ether/ether (4:1), filtered through a pad of silica gel to decolorize the solution, and washed with the same solvent mixture. After concentration, the oil was taken up in petroleum ether/ether and slowly cooled to yield 6.83 g of **1c** (83%) as a white crystalline solid: mp 71.5–72.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (br d, *J* = 8.2 Hz, 1 H, aromatic H's), 7.31 (br d, *J* = 8.2 Hz, 1 H, aromatic H's), 6.65 (d, *J* = 15.9 Hz, 1 H, C*H*CHCO$_2$R) 5.55 (d, *J* = 15.9 Hz, 1 H, CHC*H*CO$_2$R), 3.97 (t, *J* = 7.3 Hz, 2 H, CH_2CH_2O), 2.41 (s, 3 H, $CH_3C_6H_4$), 1.72 (t, *J* = 7.3 Hz, 2 H, CH_2CH_O), 1.45 (s, 9 H, $C(CH_3)_3$), 1.00 (s, 6 H, $(CH_3)_2$); ^{13}C (100.4 MHz, $CDCl_3$), δ 165.5, 154.2, 144.4, 132.8, 129.5, 127.6, 120.2, 80.3, 67.7, 40.4, 35.7, 28.3, 26.8, 21.6; IR (CCl_4) 2960, 1715, 1650, 1370, 1180, 1150 cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_5S$: C, 61.93; H, 7.66. Found: C, 61.97; H, 7.57.

(1*S,5*S**,6*S**,7*R**)-4,4-Dimethyltricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylic Acid, *tert*-Butyl Ester (12).** To a 0 °C solution of 4.7 g of **1c** (12.8 mmol) in 25 mL of dry, deoxygenated THF was slowly added a solution of 25.7 mmol of CpMgCl in 75 mL of THF. The reaction mixture was stirred 3 h at 0 °C and then for 1 h at room temperature. After dilution with 100 mL of ether, the mixture was poured into 800 mL of petroleum ether. This solution was filtered through a pad of silica gel and washed through with petroleum ether/ether (4:1). The resulting solution was concentrated to an oil and then taken up in 500 mL of benzene and 50 mg of hydroquinone. The solution was slowly heated to 75 °C over the period of 1 h and then heated at that temperature for 4 h. After being cooled to room temperature, the reaction mixture was decolorized by filtration through silica gel and washed through with benzene. VPC analysis at 140 °C revealed two cycloaddition products of t_R 4.32 min (91%) and t_R 5.88 min (9%). After removal of the volatiles, the resulting oil was taken up in 500 mL of ether, concentrated to a colorless oil, which still contained traces of ether, and allowed to stand for 24 h exposed to atmosphere. At this time the product at t_R 5.88 min was absent. The oil was distilled (Kugelrohr, 75 °C, 0.001 mmHg) to yield 2.73 g of **12** (81%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (d, *J* = 5.6 Hz, 1 H), 5.99 (dd, *J* = 2.7, 5.6 Hz, 1 H), 3.10 (br s, 1 H), 2.79 (dd, *J* = 3.4, 5.6 Hz, 1 H, 1.79–1.89 (m, 1 H), 1.58–1.74 (m, 3 H), 1.51–1.56 (m, 1 H), 1.39 (s, 9 H), 1.37–1.41 (m, 1 H), 1.14 (ddd, *J* = 1.8, 1.8, 8.1 Hz, 1 H), 1.04 (s, 3 H), 1.02 (s, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 174.1, 142.0, 132.6, 79.6, 64.9, 61.3, 50.9, 47.8, 47.5, 44.4, 36.9, 32.8, 28.4, 27.8, 26.7; IR (neat) 2960, 2870, 1730, 1455, 1365, 1150 cm^{-1}. Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.82; H, 9.99. Found: C, 77.97; H, 9.94.

(*E*)-6-[[(4-Methylphenyl)sulfonyl]oxy]hex-2-enoic Acid, Ethyl Ester (16a). A suspension of oil-free NaH (0.528 g, 22.0 mmol) in 20 mL of dry, deoxygenated benzene was cooled to 0 °C. To this suspension was slowly added 4.4 mL (22.0 mmol) of triethyl phosphonoacetate via syringe. The reaction mixture was stirred for an additional 15 min, warmed to room temperature, and then stirred at ambient temperature for 30 min. A solution

of **14a** 3.45 g, 20.0 mmol) in 14 mL of benzene was slowly added to the mixture at such a rate so as not to exceed an internal reaction temperature of 35 °C. After the addition was complete, the reaction was stirred an additional 10 h at room temperature. After quenching the reaction mixture with H_2O, the organics were extracted with Et_2O. The organics were washed with H_2O and saturated aqueous NaCl and dried over $MgSO_4$. The mixture was filtered through a pad of silica gel, washed through with Et_2O, and concentrated in vacuo to yield a colorless oil. The oil was dissolved in 125 mL of EtOH containing 0.525 g of pyridinium *p*-toluenesulfonate and then heated to 60 °C for 10 h. After the solution was cooled to room temperature, $NaHCO_3$ was added and the mixture was concentrated in vacuo at ambient temperature. The mixture was diluted with Et_2O, filtered through a pad of silica gel, and thoroughly washed through with Et_2O. The solution was concentrated in vacuo until no EtOH remained. This oil was taken up in 50 mL of dry pyridine and cooled to 0 °C. To this pyridine solution was added 5.72 g (30.0 mmol) of *p*-toluenesulfonyl chloride. The reaction was stirred at 0 °C for 20 h and was then quenched with H_2O. The mixture was extracted three times with Et_2O. The combined organics were washed with 1 N HCl until the washings were acidic and then washed with H_2O, followed by washing with saturated aqueous $NaHCO_3$ and then a saturated solution of NaCl. The organics were then dried over $MgSO_4$. Once dry, the mixture was concentrated to an oil in vacuo and purified by flash chromatography. The tosylate eluted with an R_f of 0.21 with petroleum ether/ether (3:2) and was collected and concentrated in vacuo to yield 3.87 g of **16a** (62%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2 H, aromatic H's), 7.32 (d, J = 8.0 Hz, 2 H, aromatic H's), 6.79 (td, J = 6.9, 15.6 Hz, 1 H, C*H*CHCO$_2$R), 5.70 (td, J = 1.6, 15.6 Hz, 1 H, CHC*H*CO$_2$R), 4.14 (q, J = 7.1 Hz, 2 H, OC*H*$_2$CH$_3$), 4.01 (t, J = 6.4 Hz, 2 H, OC*H*$_2$CH$_2$), 2.42 (s, 3 H, C*H*$_3$C$_6$H$_4$), 2.22 (ddt, J = 1.6, 6.9, 7.0 Hz, 2 H, CH$_2$C*H*$_2$CH), 1.78 (m, 2 H, CH$_2$C*H*$_2$CH$_2$), 1.25 (t, J = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 165.7, 146.1, 144.5, 132.8, 129.6, 127.6, 122.3, 69.2, 60.3, 28.1, 27.5, 21.9, 14.5; IR (neat) 1731, 1600 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_2S$: C, 57.67; H, 6.45. Found: C, 57.61; H, 6.53.

Reaction of CpMgCl with 16a. To 204 mg (0.653 mmol) of **17a** in 4.0 mL of dry THF at −40 °C was added a solution of 272 mg (0.718 mmol) of CpMgCl in 3.0 mL of THF. The reaction mixture was allowed to warm to room temperature over the period of 1 h, was diluted with petroleum ether, and was filtered through a pad of silica gel. The resulting solution was concentrated to an oil, taken up in 25 mL of benzene, and heated for 10 h at reflux. By filtering the reaction mixture through silica gel, the solution was decolorized. VPC analysis of 120 °C revealed the presence of two products at t_R 3.99 min (3%) and t_R 4.35 min (87%). Infrared analysis showed the presence of an ester carbonyl (1732 cm^{-1}) that was not α,β-unsaturated. ^{1}H NMR (400 MHz, $CDCl_3$) showed only the presence of an almost equal mixture of **20** and **21**. The cycloaddition product was not observed due to the relatively small amounts that were present with respect to **20** and **21**: ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 175.7, 150.6, 148.6, 133.7, 133.0, 131.9, 125.8, 125.1, 60.31, 60.29, 51.0, 50.1, 45.8, 44.6, 42.1, 41.2, 34.0, 32.9, 31.8, 30.8, 30.7, 25.1, 24.9, 22.9, 14.5, 14.4.

(*E*)-6-[[(4-Methylphenyl)sulfonyl]oxy]hex-2-enoic Acid, *tert*-Butyl Ester (16b). Prepared as for **16a**. The tosylate eluted with an R_f of 0.22 with petroleum ether/ether (2:1) to give 4.50 g (78% overall) of the tosylate **16b** as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (br d, J = 8.2 Hz, 2 H, aromatic H's), 7.35 (br d, J = 8.2 Hz, 2 H, aromatic H's), 6.72 (td, J = 6.8, 15.6 Hz, 1 H, C*H*CHCO$_2$R), 5.67 (td, J = 1.6 Hz, 1 H, CHC*H*CO$_2$R), 4.04 (t, J = 6.2 Hz, 2 H, OC*H*$_2$), 2.45 (s, 3 H, C*H*$_3$C$_6$H$_4$), 2.21 (dtd, J = 1.6, 6.6, 6.8 Hz, 2 H, CH$_2$C*H*$_2$CH), 1.78 (tt, J = 6.2, 6.6 Hz, 2 H, CH$_2$C*H*$_2$CH$_2$), 1.47 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 164.8, 144.6, 144.2, 132.5, 129.3, 127.2, 123.7, 79.8, 69.1, 28.0, 27.6, 27.3, 21.5; IR (neat) 2980, 1711, 1658, 1601 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_5S$: C, 59.98; H, 7.11. Found: C, 59.87; H, 6.99.

Reaction of CpMgCl with 16b. To 170 mg (0.500 mmol) of **16b** in 3.0 mL of dry THF at room temperature was added a solution of 227 mg (0.540 mmol) of CpMgCl in 3.0 mL of THF. The reaction mixture was stirred at room temperature for 15 min, diluted with petroleum ether, and filtered through a pad of silica gel. The solution was concentrated to an oil, taken up in 25 mL of benzene, and heated at reflux for 12 h. VPC analysis at 120 °C showed two products at t_R 3.48 min (4%) and t_R 4.19 min (96%). ^{1}H NMR (400 MHz, $CDCl_3$) showed the major VPC peak to result from two isomers of a monosubstituted cyclopentadiene. The minor compound appeared to be **26** by the characteristic peaks at δ 6.20 (d, J = 5.6 Hz, 1 H) and 5.91 (dd, J = 2.7, 5.6 Hz, 1 H). There was no tosylate functionality observed. The reaction of half of the reaction mixture with 0.250 mmol of maleic anhydride caused the disappearance of only the peak at t_R 4.19 min by VPC analysis.

(*E*)-7-[[(4-Methylphenyl)sulfonyl]oxy]hept-2-enoic Acid, *tert*-Butyl Ester (16c). Via a procedure only slightly modified from that for **16b**, **16c** was prepared with 3.50 g (18.8 mmol) of **14c** as starting material. The aldehyde was added to the phosphonate anion as previously described and allowed to react for 8 h at room temperature before standard workup. Removal of the tetrahydropyran protecting group was achieved as before, and the alcohol was purified by flash chromatography. Elution on silica gel with petroleum ether/ether (1:1) produced 3.34 g (89%) of a colorless oil with R_f 0.35. Transformation of the alcohol to the tosylate was complete within 20 h, and standard workup produced crude **16c**. Isolation was achieved through the use of flash chromatography. The tosylate eluted with R_f 0.31 with petroleum ether/ether (3:1) to give 4.87 g (73% overall) of **16c** as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (br d, J = 7.8 Hz, 2 H, aromatic H's), 7.36 (br d, J = 7.8 Hz, 2 H aromatic H's), 6.76 (td, J = 6.8, 15.6 Hz, 1 H, C*H*CHCO$_2$R), 5.69 (td, J = 1.6, 15.6 Hz, 1 H, CHCH*H*CO$_2$R), 4.03 (t, J = 6.4 Hz, 2 H, OC*H*$_2$), 2.45 (s, 3 H, C*H*$_3$C$_6$H$_4$), 2.12 (ddt, J = 1.6, 6.8, 6.8 Hz, 2 H, CH$_2$C*H*$_2$CHCH), 1.62–1.72 (m, 2 H, OCH$_2$C*H*$_2$), 1.42–1.52 (m, 2 H, OCH$_2$CH$_2$C*H*$_2$), 1.48 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 165.0, 145.9, 144.18 132.5, 129.3, 127.2, 123.1, 79.7, 69.7, 31.0, 28.1, 28.0, 23.8, 21.5; IR (neat) 2980, 2935, 1710, 1655, 1600 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_5S$: C, 60.99; H, 7.39. Found: C, 60.96; H, 7.30.

(*E*)-5-[[(4-Methylphenyl)sulfonyl]oxy]pent-2-enoic Acid, *tert*-Butyl Ester (16d). Via a procedure only slightly modified from that for **16b**, **16d** was prepared with 1.41 g (8.9 mmol) of **14d** as starting material. The aldehyde was added to the phosphonate anion as previously described and allowed to react for 1 h at room temperature before standard workup. Removal of the tetrahydropyranyl protecting group was achieved as before, and the alcohol was purified by flash chromatography. Elution on silica gel with ether/petroleum ether (3:2) produced 1.26 g (82%) of a colorless oil with R_f −0.25. Transformation of the alcohol to the tosylate was complete within 20 h, and standard workup produced crude **16d**, which was purified by flash chromatography. The tosylate eluted with R_f 0.23 petroleum ether/ether (2:1) to give 1.86 g (64% overall) of **16d** as a colorless oil, which solidified over several days. Crystals were obtained with use of ether/pentane: mp 76.0–77.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (br d, J = 8.3 Hz, 2 H, aromatic H's), 7.32 (br d, J = 8.3 Hz, 2 H, aromatic H's), 6.62 (td, J = 6.8, 15.9 Hz, 1 H, C*H*CHCO$_2$R), 5.72 (td, J = 1.5, 15.9 Hz, 1 H, CHC*H*CO$_2$R), 4.07 (t, J = 6.5 Hz, 2 H, OCH$_2$), 2.48 (dtd, J = 1.5, 6.5, 6.8 Hz, 2 H, OCH$_2$C*H*$_2$), 2.42 (s, 3 H, C*H*$_3$C$_6$H$_4$), 1.44 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 164.7, 144.6, 140.4, 132.6, 129.6, 127.6, 125.9, 80.4, 68.1, 31.6, 28.3, 21.9; IR (neat) 2975, 2925, 1713, 1658, 1601 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_5S$: C, 58.88; H, 6.79. Found: C, 59.13; H, 7.03.

(*E*)-6-Iodohex-2-enoic Acid, *tert*-Butyl Ester (17b). A solution of 1.66 g of **16b** (4.6 mmol) and 2.19 g of NaI (14.6 mmol) in dry acetone was heated to 45 °C under argon atmosphere and allowed to stir for 2 h. After the mixture had cooled to room temperature, the mixture was concentrated in vacuo. The resulting slush was taken up in ether, filtered through a pad of silica gel, and washed through the ether. Concentration of the organics produced a yellow oil. Distillation of this oil (Kugelrohr, 65–70 °C, 0.1 mmHg) produced 1.40 g of **17b** (97%) of a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (td, J = 7.1, 15.6 Hz, 1 H, C*H*CHCO$_2$R), 5.80 (td, J = 1.7, 15.6 Hz, 1 H, CHC*H*CHO$_2$R), 3.19 (t, J = 6.8 Hz, 2 H, IC*H*$_2$), 2.30 (ddt, J = 1.7, 7.1, 7.1 Hz, 2 H, ICH$_2$CH$_2$C*H*$_2$), 1.97 (m, 2 H, ICH$_2$C*H*$_2$), 1.48 (s, 9 H, C(C*H*$_3$)$_3$); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 164.9, 144.5, 123.7, 79.8, 32.4, 31.4, 28.0, 5.4; IR (neat) 2980, 2935, 1720, 1660, 1370, 1165 cm^{-1}. Anal. Calcd for $C_{10}H_{17}IO_2$: C, 40.56; H, 5.79. Found: C, 40.28; H, 5.71.

(*E*)-7-Iodohept-2-enoic Acid, *tert*-Butyl Ester (17c). By the same procedure as that outlined for the preparation of **17b**, 2.98 g of **16c** (8.42 mmol) was transformed into the crude iodide **17c** (96%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (td, J = 6.9, 15.5 Hz, 1 H, C*H*CHCO$_2$R), 5.75 (td, J = 1.6, 15.5 Hz, 1 H, CHC*H*CO$_2$R), 3.19 (t, J = 7.1 Hz, 2H, ICH_2), 2.20 (ddt, J = 1.6, 6.9, 6.9 Hz, 2 H, CH$_2$CH_2CHCH), 1.80–1.90 (m, 2 H, ICH$_2$CHH_2), 1.44–1.64 (m, 2 H, ICH$_2$CH$_2$CH_2), 1.48 (s, 9 H, C(CH_3)$_3$); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 165.1, 146.1, 123.0, 79.8, 32.6, 30.7, 28.8, 28.0, 6.1; IR (neat) 2980, 2935, 1712, 1658, 1370, 1165 cm^{-1}. Anal. Calcd for $C_{11}H_{19}IO_2$: C, 42.60; H, 6.17. Found: C, 42.41; H, 6.12.

(1*R,5*S**,6*R**,7*S**)-Tricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylic Acid, *tert*-Butyl Ester (26) and (1*R**,7*R**,8*R**,10*R**)-Tricyclo[5.2.1.0^{3,8}]dec-2-ene-10-carboxylic Acid, *tert*-Butyl Ester (27).** To 296 mg of **17b** (1.00 mmol) in 5.0 mL of dry THF at 0 °C was slowly added to 4.0 mL of 0.25 M CpMgCl (1.00 mmol) in THF. The reaction was stirred at 0 °C for 1 h and then allowed to warm to room temperature over the period of 1.5 h. The reaction mixture was diluted with 40 mL of hexane, filtered through a silica gel pad, and then washed with petroleum ether/ether (4:1). After concentration of the solution, the nonvolatile compounds were taken up in 60 mL of benzene and 5 mg of hydroquinone and heated to reflux. Reflux was maintained for 2 h. VPC analysis at 120 °C showed three products with t_R 4.07 (75%), 4.84 (14%), and 5.10 min (12%). The solution was concentrated with reduced pressure to a volume of 5 mL, and 20 mg of maleic anhydride (0.20 mmol) was added with stirring. The mixture was allowed to react for 2 h at ambient temperature at which time the product of t_R 4.84 min was absent. The reaction mixture was concentrated in vacuo, and isolation of the two two products was achieved by flash chromatography. Elution on silica gel with petroleum ether/ether (40:1) produced 160 mg of **26** (68%) of R_f 0.23 and 14 mg of **27** (6%) of R_f 0.26.

26: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (d, J = 5.6 Hz, 1 H), 5.91 (dd, J = 2.7, 5.6 H, 1 H), 3.13 (br s, 1 H), 2.63 (dd, J = 3.8, 3.8 Hz, 1 H), 2.00–2.10 (m, 1 H), 1.78–1.96 (m, 4 H), 1.60–1.72 (m, 1 H), 1.35–1.44 (m, 1 H), 1.38 (s, 9 H), 1.20–1.30 (m, 2 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 173.5, 141.6, 132.0, 79.6, 63.8, 52.4, 52.1, 50.3, 49.4, 31.2, 28.3, 27.1, 27.0; IR (neat) 3060, 2980, 2880, 1730, 1565, 1460, 1370, 1150 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.72; H, 9.33.

27: ^{1}H NMR (400 MHz, $CDCl_3$), assignment as in Figure 2, δ 5.55 (br s, 1 H, H_1), 3.00 (br s, 1 H, H_2), 2.57–2.62 (m, 1 H, H_3), 2.50–254 (m, 1 H, H_4), 2.32 (ddd, J = 2.0, 5.9, 11.5 Hz, 1 H, H_5), 2.03 (ddd, J = 4.6, 11.4 Hz, 1 H, H_6), 1.69–1.79 (m, 1 H, H_7), 1.71 (dd, J = 1.2, 3.7 Hz, 1 H, H_8), 1.35–1.65 (m, 3 H, H_9, H_{10}, H_{11}), 1.42 (s, 9 H, H_{12}), 1.14–1.32 (m, 2 H, H_{13}, H_{14}); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 174.4, 149.1 128.7, 79.8, 51.9, 50.3, 50.2, 43.8, 40.3, 30.3, 30.0, 28.4, 27.1; IR (neat) 2940, 2860, 1728, 1600, 1370, 1165, 1150 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.45; H, 9.70.

Cycloaddition of 22 at 23 °C. To 296 mg of **17b** (1.00 mmol) in 5.0 mL of dry THF at 0 °C was added 4.0 mL of 0.25 M CpMgCl (1.00 mmol) in THF. After being stirred for 1 h at 0 °C, the reaction mixture was diluted with 50 mL of petroleum ether. The mixture was filtered through a silica gel pad and washed through with petroleum ether/ether (4:1). The concentration of the solution to a colorless oil was achieved in vacuo at or below room temperature. The mixture was then taken up in 100 mL of benzene and 5 mg of hydroquinone and allowed to stand 4 days at room temperature. An aliquot of the solution was concentrated in vacuo and taken up in C_6D_6. ^{1}H NMR showed the cycloaddition to be greater than 95% complete. By integration of the olefin resonances, the ratio of **26** to **27** was established as greater than 98:2. After the addition of 3 mg of maleic anhydride, the sample was allowed to stand for 2 h. Analysis of the sample by capillary gas chromatography revealed at 98.5:1.5 ratio of **26** to **27**.

Cycloaddition of 23 Catalyzed by Et_2AlCl at −15 °C. To 296 mg of **17b** (1.00 mmol) in 5.0 mL of dry THF at 0 °C were slowly added 4.0 mL of 0.25 M CpMgCl (1.00 mmol) in THF. After being stirred for 1 h at 0 °C, the reaction mixture was diluted with 50 mL of petroleum ether. The mixture was filtered through a silica gel pad and washed through with petroleum ether/ether (4:1). Concentration of the solution to a colorless oil was achieved in vacuo at or below room temperature. The mixture was taken up in 15 mL of ether and allowed to stand 4 h at room temperature. The ether was then removed in vacuo and replaced with 15 mL of dry, deoxygenated methylene chloride. After the mixture was cooled to −78 °C, 78 μL of 1.8 M Et_2AlCl (1.4 mmol) was added slowly via syringe and stirred 15 min at −78 °C. The reaction mixture was warmed to −15 °C (ethylene glycol, CO_2) and stirred for 5 h. Over an additional 10 h, the solution was allowed to warm to 15 °C. The reactions was quenched with saturated aqueous ammonium chloride and extracted with ether. Analysis by capillary gas chromatography revealed the only cycloaddition product to be **26**: **27** was not detected.

(1*R,6*S**,7*R**,8*S**)-Tricyclo[6.2.1.0^{1,6}]undec-9-ene-7-carboxylic Acid, *tert*-Butyl Ester (34) and (1*R**,6*R**,7*S**,8*S**)-Tricyclo[6.2.1.0^{1,6}]undec-9-ene-7-carboxylic Acid, *tert*-Butyl Ester (35).** To 310 mg of **17c** (1.00 mmol) in 5.0 mL of dry THF at 0 °C was slowly added 4.0 mL of 0.25 M CpMgCl (1.00 mmol) in THF. After being stirred for 1 h at 0 °C, the reaction was diluted with 50 mL of petroleum ether. The mixture was filtered through a silica gel pad and washed through with petroleum ether/ether (4:1). Concentration of the solution in vacuo produced a colorless oil. Cycloaddition was accomplished by dissolving the mixture in 50 mL of benzene and 5 mg of hydroquinone. The solution was brought to reflux for 4 h and then cooled to room temperature. Analysis of the mixture by capillary gas chromatography at 125 °C revealed the presence of three products with t_R 4.83 (28%), 5.21 (63%), and 5.34 min (9%). The solution was concentrated in vacuo to a volume of 5 mL, and 20 mg of maleic anhydride (0.20 mmol) was added with stirring. The mixture was allowed to react for 3 h at ambient temperature at which time the product of t_R 5.34 was absent. The reaction mixture was concentrated in vacuo, and isolation of the two products was achieved by flash chromatography. Elution on silica gel with petroleum ether/ether (40:1) produced 43 mg of **35** (17%) of R_f 0.29 and 99 mg of **34** (40%) of R_f 0.24.

34: ^{1}H NMR (400 MHz, $CDCl_3$), assignments as in Figure 3, δ 5.99 (dd, J = 2.9, 5.6 Hz, 1 H, H_1), 5.85 (d, J = 5.6 Hz, 1 H, H_2), 2.99 (br s, 1 H, H_3), 2.36 (dd, J = 3.8, 3.8 Hz, 1 H, H_4), 2.05–2.13 (m, 1 H, H_5), 1.88 (br d, J = 12.2 Hz, 1 H, H_6), 1.62–1.78 (m, 4 H, H_7, H_8, H_9, H_{10}), 1.30–1.46 (m, 1 H, H_{11}), 1.38 (s, 9 H, H_{12}), 1.16–1.30 (m, 2 H, H_{13}, H_{14}), 1.12–1.16 (m, 2 H, H_{15}, H_{16}); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 173.4, 143.0, 133.5, 79.5, 54.8, 53.0, 48.3, 46.4, 41.9, 33.4, 30.0, 28.4, 26.5, 23.6; IR (neat) 2980, 2925, 2860, 1726, 1370, 1370, 1255, 1160, 1150 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.44; H, 10.00.

35: ^{1}H NMR (400 MHz, $CDCl_3$), assignments as in Figure 4, δ 6.23 (dd, J = 3.2, 5.6 Hz, 1 H, H_1), 6.01 (d, J = 5.6 Hz, 1 H, H_2), 2.77–2.81 (m, 1 H, H_3), 1.92–1.99 (m, 1 H, H_4), 1.65–1.80 (m, 6 H), 1.43 (s, 9 H, C(CH_3)$_3$), 1.34 (br d, J = 8.30 Hz, 1 H, H_7), 1.20–1.53 (m, 3 H), 0.75 (m, 1 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 175.2, 137.1, 137.0, 79.7, 53.3, 52.6, 52.2, 48.5, 46.7, 30.8, 28.4, 27.1, 24.0; IR (neat) 2975, 2920, 2850, 1730, 1365, 1150, 1125 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.34; H, 9.67.

Cycloaddition of 31 Catalyzed by Et_2AlCl at −15 °C. The coupling of CpMgCl and **17c** was performed as before. The mixture of substituted cyclopentadienes was taken up in 15 mL of ether and allowed to stand 4 h at room temperature. The ether was then removed in vacuo and replaced with 15 mL of dry, deoxygenated methylene chloride. After the mixture was cooled to −78 °C, 78 μL of 1.8 M Et_2AlCl (1.4 mmol) was added slowly via syringe and stirred for 15 min at −78 °C. The reaction was warmed to −15 °C (ethylene glycol, CO_2) and stirred for 12 h at −15 °C. The reaction was quenched with saturated ammonium chloride, and extracted with ether. VPC analysis revealed the ratio of **34** to **35** to be 73:27.

(1*R,2*S**,3*R**,6*S**)-Tricyclo[4.3.0.0^{3,7}]non-4-ene-2-carboxylic Acid, *tert*-Butyl Ester (40).** To 282 mg of **17d** (1.00 mmol) in 5.0 mL of dry THF at 0 °C was slowly added 4.0 mL of 0.25 M CpMgCl (1.00 mmol) in THF. After being stirred for 1 h at 0 °C, the reaction mixture was diluted with 50 mL of petroleum ether. The mixture was filtered though a silica gel pad and washed with petroleum ether/ether (4:1). Concentration of the solution in vacuo produced a colorless oil. Cycloaddition was accomplished by dissolving the mixture in 120 mL of dry, de-

oxygenated toluene and 5 mg of hydroquinone. The reaction mixture was heated to reflux under an argon atmosphere and maintained at reflux for 18 h. Analysis of the mixture by capillary gas chromatography at 120 °C revealed the presence of two products with t_R 3.10 (78%) and 3.41 min (22%). The solution was concentrated to a volume of 5 mL, and 40 mg of maleic anhydride (0.40 mmol) was added with stirring. The mixture was allowed to react for 2 h at ambient temperature at which time the product with t_R 3.41 min was absent. The reaction mixture was concentrated in vacuo, and isolation of the product was achieved by flash chromatography. Elution on silica gel with petroleum ether/ether (40:1) produced 116 mg (53%) of **40** with R_f 0.18 as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$), assignments as in Figure 5, δ 6.04 (dd, J = 2.9, 5.6 Hz, 1 H, H_1), 5.86 (dd, J = 2.7, 5.6 Hz, 1 H, H_2), 2.83–2.88 (m, 1 H, H_3), 2.57 (br s, 1 H, H_4), 2.37(d, J = 4.9 Hz, H_5), 2.18–2.26 (m, 2 H, H_6, H_7), 1.65–1.80 (m, 2 H, H_8, H_9), 1.33–1.48 (m, 1 H, H_{10}), 1.37 (s, 9 H, H_{11}), 1.13–1.23 (m, 1 H, H_{12}); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 172.6, 133.7, 132.9, 79.6, 63.1, 53.1, 50.8, 50.2, 38.9, 34.4, 28.4, 22.1; IR (neat) 3060, 2975, 2870, 1733, 1370, 1240, 1160, 1120 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.12; H, 9.16.

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Registry No. **1c**, 117471-71-3; **2**, 117471-72-4; **9**, 3709-08-8; **10**, 102536-89-0; **11**, 117471-73-5; **12**, 117557-95-6; **13**, 117471-74-6; **14a**, 54911-85-2; **14c**, 14194-86-6; **14d**, 62592-78-3; **15a**, 96251-91-1; **15c**, 117471-84-8; **15d**, 117471-86-0; **16a**, 117471-75-7; **16b**, 117471-82-6; **16c**, 117471-83-7; **16d**, 117471-85-9; **17a**, 64277-92-5; **17b**, 117471-87-1; **17c**, 117471-88-2; **17d**, 117471-89-3; **20**, 117471-76-8; **21**, 117471-77-9; **23**, 117471-92-8; **26**, 117471-78-0; **27**, 117471-79-1; **31**, 117471-91-7; **34**, 117471-80-4; **35**, 117557-96-7; **37**, 117471-90-6; **40**, 117471-81-5; CpMgBr, 34766-86-4; CpMgCl, 34766-85-3; $(EtO)_2POCH_2CO_2C(CH_3)_3$, 27784-76-5; γ-butyrolactone, 96-48-0; cyclopentadiene, 542-92-7; triethyl phosphonoacetate, 867-13-0.

Reductive Addition of Polyhalomethanes and Their Related Compounds to Aldehydes and 1,2-Elimination of the Coupling Products in a Pb/Al Bimetal Redox System

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A Pb/Al bimetal system was used to carry out reductive addition of tetrachloromethane, tetrabromomethane, bromotrichloromethane, trichloroacetamide, and trichloroacetonitrile to aldehydes. Subsequent 1,2-elimination of the halogen atom and hydroxyl group from the coupling products was also performed with the Pb/Al bimetal system. The technology was successfully applied to stereocontrolled syntheses of ethyl *trans*- and *cis*-3-(2,2-dihaloethenyl)-2,2-dimethylcyclopropanecarboxylates.

Reductive addition of polyhaloalkanes to carbonyl compounds is important for making carbon–carbon bonds in organic synthesis, and various kinds of low-valent metals have been employed for this purpose.[1] Although the reductive addition of tetrahalomethanes to aldehydes provides direct access to trihalomethyl carbinols, very few metals are known to be effective in such reactions, presumably due to the instability of intermediary metal carbenoids.[2] To our knowledge, the reductive addition of tetrabromomethane to aldehydes with SnF_2[3] is the only example hitherto disclosed.

Base-induced addition of chloroform to aldehydes has been studied as a route to trichloromethyl carbinols,[4,5] but the yields of the trichloromethyl carbinols often suffer due to undesirable side reactions. The reaction of aromatic

Scheme I

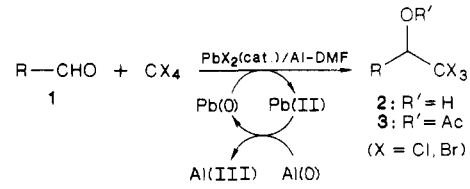

Table I. Effect of Metal Salts in the Reductive Addition of CCl_4 to Aldehyde 1a[a]

entry	metal salt, mmol	time, h	yield,[b] %
1	$PbBr_2$ (0.1)	3	94
2	$PbCl_2$ (0.1)	3.5	97
3	Pb (0.1)	5	95
4	none	10	– (93[c])
5	$SnCl_2$ (0.1)	12	– (98[c])
6	$SnCl_2$ (0.5)	5	92
7	$BiCl_3$ (0.1)	10	– (98[c])
8	$GeCl_4$ (0.1)	10	– (91[c])
9	$ZnCl_2$ (0.1)	10	– (88[c])

[a] Carried out with **1a** (1 mmol), CCl_4 (2 mmol), and Al (1.2 mmol) in DMF (5 mL) at room temperature. [b] Isolated yields based on aldehyde **1a**. [c] Recovered **1a**.

(1) (a) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769. (b) Villieras, J.; Bacquet, C.; Normant, J. F. *J. Organomet. Chem.* **1975**, *97*, 325. (c) Santini, G.; Le Blanc, M.; Riess, J. G. *J. Chem. Soc., Chem. Commun.* **1975**, 678. (d) Furet, C.; Servens, C.; Pereyre, M. *J. Organomet. Chem.* **1975**, *102*, 423. (e) Fujita, M.; Morita, T.; Hiyama, T. *Tetrahedron Lett.* **1986**, *27*, 2135 and references cited therein.

(2) (a) Haszeldine, R. N. *J. Chem. Soc.* **1954**, 1273. (b) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971. (c) Taguchi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 3010.

(3) Mukaiyama, T.; Yamaguchi, M.; Kato, *J. Chem. Lett.* **1981**, 1505.

(4) Addition by use of chemical bases: (a) Weizmann, Ch.; Bergmann, E.; Sulzbacher, M. *J. Am. Chem. Soc.* **1948**, *70*, 1189. (b) Bergmann, E. D.; Ginsburg, D.; Lavie, D. *Ibid.* **1950**, *72*, 5012. (c) Kaspar, E.; Wiechert, R. *Chem. Ber.* **1958**, *91*, 2664. (d) Merz, A.; Tomahogh, R. *Ibid.* **1977**, *110*, 96 and references cited therein.

0022-3263/89/1954-0444$01.50/0