of the diastereotopic olefin faces.

Diastereoselection. In general, good levels of diastereoselection were achieved in the hydroboration of α-alkoxy-β,γ-unsaturated methyl esters with preference for the formation of the 2,3-anti product (entries 1–7). In contrast, the α-methyl-β,γ-unsaturated ester **1h** (entry 8) afforded a statistical mixture of all possible isomers. Without activation of the ester moiety by the alkoxy group, the intermolecular olefin hydroboration pathway competes with ester reduction resulting in a complete loss of selectivity (entries 8, 9). The predominant formation of the 2,3-anti-diastereomer is consistent with that expected for an intramolecular hydroboration of chiral homoallylic alcohols and is opposite to the model proposed by Kishi for intermolecular hydroboration of chiral allylic ethers.[18] The data obtained from these experiments indicate that the relative stereochemistry of the alkoxy substituent between the ester group and the double bond does not affect the sense of diastereoselection. For the cases shown in Table I, the hydroboration reactions of α-alkoxy esters proceded in a stereochemically consistant manner. The production of the 2,3-anti diastereomer is independent of the existing relative stereochemical relationships. The all syn-substrates showed slightly higher selectivity than the anti diastereomers. For instance, the syn and anti diastereomers **1b** and **1c** are converted to the 2,3-anti diols with 1.05 equiv of $BH_3{\cdot}SMe_2$ with ratios of 7:1–4:1, respectively. The difference in the stereoselectivity observed in the hydroboration reactions maybe a function of the degree of $A^{1,3}$ strain associated with the respective double-bond rotamers in the transition states, ΔG^{*} $TS_B > \Delta G^{*}$ TS_A (Scheme I). It is interesting to note that the size of the alkoxy substituent does not effect the selectivity as shown with α-methoxy and benzyloxy groups; compare entries 1 and 2 with 4.

In summary, we have shown that borane methyl sulfide is an effective reagent for the sequential reduction–hydroboration of α-alkoxy-β,γ-unsaturated methyl esters affording 1,3-diols with useful levels of selectivity. With the data obtained from these initial experiments four lines of evidence have emerged supporting the notion of a heteroatom-directed hydroboration: (i) prior ester reduction, (ii) opposite sense of diastereoselection is obtained from that which is expected from an intermolecular hydroboration of an allylic ether,[18,19] (iii) the isolation and characterization of cyclic boronates **3a,b** and **4a**, and (iv) nonselective hydroboration of the homoallylic TBDMS ether derivative **6**. The observations cited above support the assertion that the hydroboration is alkoxy directed however, the implication of a dialkoxy borane as the effective hydroborating agent is in opposition to conventional wisdom that alkoxy boranes are too unreactive to hydroborate olefins. Further studies and applications concerning the alkoxy-directed hydroboration are in progress and will reported in due course.

Acknowledgment. This work has been financially supported by the National Institutes of Health (CA47249).

Supplementary Material Available: Experimental procedures and spectral data for all reaction products as well as relative stereochemical proof of the major and minor 1,3-diols (7 pages). This material is contained in many 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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Catalytic Chromium(0)-Promoted Higher-Order Cycloaddition Reactions

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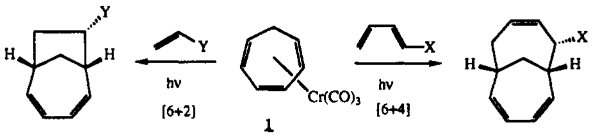
Received June 29, 1992

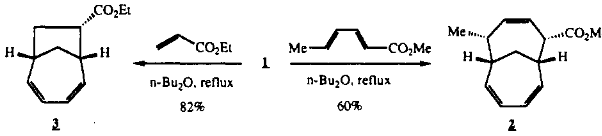
Summary: Transition-metal-promoted [$6\pi + 4\pi$] and [$6\pi + 2\pi$] higher-order cycloaddition reactions can be effected thermally or by employing a chromium metal catalyst. The resultant products are identical in all respects to those generated photochemically.

Recently, we[1] and others[2] have reported that a variety of transition-metal π complexes can be induced to undergo smooth and efficient higher-order cycloaddition via photochemical activation (eq 1). The resultant adducts are particularly rich in stereochemical information and may serve as useful building blocks for natural product synthesis.



(1)

We now wish to disclose that thermal activation of (η^6-cycloheptatriene)tricarbonylchromium(0) (1) and related complexes in the presence of appropriate 4π and 2π partners also provides [6 + 4] and [6 + 2] cycloadducts, respectively, which are identical in all respects to those derived from the photoinduced process (eq 2). Furthermore, we have demonstrated that these same transformations can also be effected employing only a catalytic quantity of the transition metal.



(2)

The stoichiometric, thermal versions of these reactions can be achieved by simply heating a mixture of complex

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[1] (a) Rigby, J. H.; Henshilwood, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 5122. (b) Rigby, J. H.; Ateeq, H. S. *Ibid.* **1990**, *112*, 6442 and references cited therein.

[2] For other recent advances in this area, see: (a) Van Houwelingen, T.; Stufkens, D. J.; Oskam, A. *Organometallics* **1992**, *11*, 1146. (b) Chaffee, K.; Sheridan, J. B.; Aistars, A. *Ibid.* **1992**, *11*, 18. (c) Fischler, I.; Grevels, F.-W.; Leitich, J.; Özkar, S. *Chem. Ber.* **1991**, *124*, 2857. (d) Kreiter, C. G.; Lehr, K.; Leyendecker, M.; Sheldrick, W. S.; Exner, R. *Ibid.* **1991**, *124*, 3. (e) Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297. (f) Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 4678.

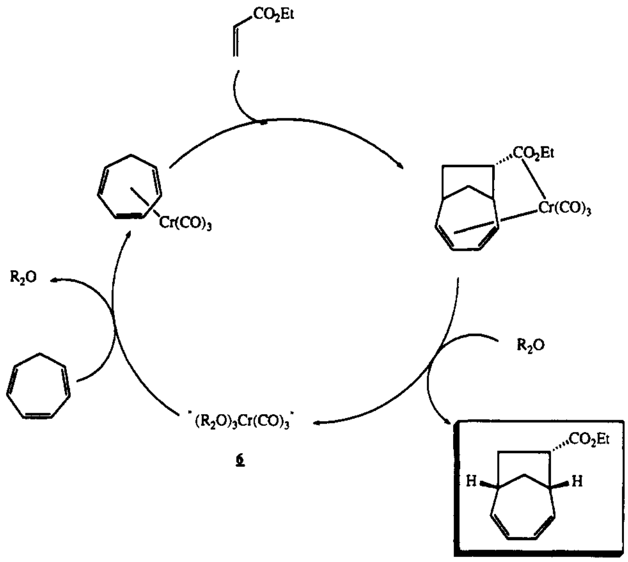
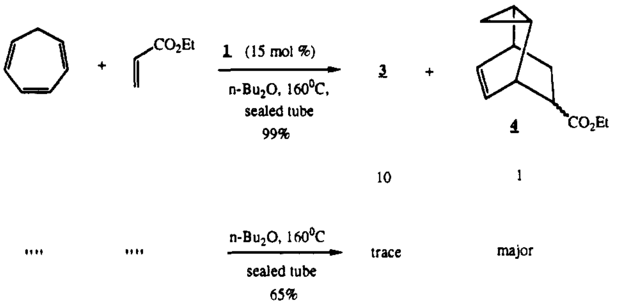


Figure 1.

1 with an excess of the 4π or 2π partner (2–10 equiv) (n-Bu_2O, reflux) for several hours.[3] The formation of adducts 2[4] and 3,[4] depicted in eq 2, are typical. In each case examined the adduct was isolated metal free as a single, endo diastereomer.[5] The production of metal-free adducts in the thermal reactions suggested the possibility of effecting these transformations using only a catalytic quantity of the "$Cr(CO)_3$" source.

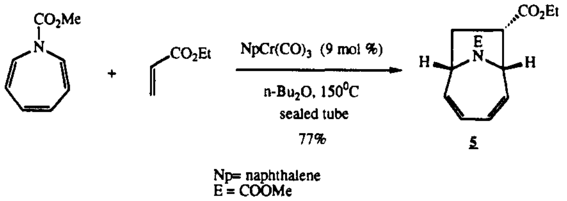


(3)

In the event, heating cycloheptatriene and excess ethyl acrylate in the presence of a catalytic amount of complex 1 (n-Bu_2O, 160 °C, sealed tube, 15 h) gave a mixture of 3 and 4[4] in a 10:1 ratio and 99% yield. It is noteworthy that thermolysis of these same reactants under identical conditions in the absence of the metal catalyst gave a 65% yield of a mixture comprised principally of 4 with only a trace of compound 3 produced.[6] *The presence of the metal catalyst completely reverses the course of this cycloaddition process.* Smaller quantities of catalyst 1 are also effective in promoting this cycloaddition with enhanced discrimination in the formation of 3 and 4. Heating cycloheptatriene and ethyl acrylate (135 °C, t-BuOMe, 20 h) in the presence of 0.02 mol equiv of 1 provided a mixture of 3 and 4 (98:2) in a 55% yield.

Interestingly, the corresponding [6 + 4] cycloaddition reactions, although much slower than the [6 + 2] version (36% conversion after 18 h), can be best effected by exposing a mixture of cycloheptatriene and the given diene partner to a catalyst in which one of the CO ligands has been replaced with Ph_3P.[7] This observation is particularly significant in that it offers the opportunity to examine a range of chiral phosphine ligands with regard to promoting asymmetric induction during the cycloaddition.

Other cyclic trienes undergo efficient catalytic metal-promoted cycloaddition as well. For example, N-(methoxycarbonyl)azepine[8] reacts with excess ethyl acrylate in the presence of 9 mol % of (η^6-naphthalene)tricarbonylchromium(0) to produce the homotropane 5[4,9] as a single diastereomer in 77% yield.



(4)

The catalytic cycle depicted in Figure 1 can satisfactorily explain many of the observations made to date. A coordinating solvent such as n-Bu_2O can serve both to initiate ligand exchange at the beginning of the process and to decomplex the resultant cycloadduct metal tricarbonyl complex and recycle the metal in the form of a very reactive "$Cr(CO)_3$" transfer agent.[10] The reduced rate of the [6 + 4] addition as compared to the [6 + 2] reaction can be rationalized in terms of the stabilities of the respective adduct–metal complexes.[11] It is worth noting that the putative "$Cr(CO)_3$" carrier 6 has also been invoked as the actual catalytic agent in the facile chromium(0)-mediated 1,4-reduction of dienes in coordinating solvents.[12]

The capability of effecting a variety of higher-order cycloaddition reactions using only catalytic quantities of the metal center will greatly expand the utility of these powerful transformations.

Acknowledgment. We thank the National Institutes of Health (GM-30771) for their generous financial support of this research.

Supplementary Material Available: Experimental procedures and compound characterization data (4 pages). This material is contained in many 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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(3) In preliminary experiments, light was rigorously excluded.

(4) This compound exhibited spectral (^1H NMR, ^{13}C NMR, IR) and analytical (combustion analysis and/or HRMS) data consistent with the assigned structure.

(5) All products from the thermal reactions were shown to be identical in all respects with the adducts prepared earlier using the photochemical procedure.[1]

(6) It is well-known that cycloadducts from norcaradiene prevail when cycloheptatriene is heated in the presence of electron-deficient 2π addends: (a) Rigby, J. H.; Denis, J.-P. *Synth. Commun.* **1986**, *16*, 1789. (b) Jenner, G.; Papadopoulos, M. *J. Org. Chem.* **1986**, *51*, 585. (c) Bellus, D.; Helferich, G.; Weis, C. D. *Helv. Chim. Acta* **1971**, *54*, 463.

(7) Anderson, W. P.; Blenderman, W. G.; Drews, K. A. *J. Organomet. Chem.* **1972**, *42*, 139.

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(10) (a) Al-Kathumi, K. M.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1974**, 428. (b) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res., Miniprint* **1979**, 1752. (c) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557.

(11) The [6 + 4] adduct–metal complexes are easily isolated from the photochemically initiated reactions,[1b] whereas the corresponding [6 + 2] adduct–metal complexes cannot be isolated under similar conditions.[1a]

(12) Yagupsky, G.; Cais, M. *Inorg. Chim. Acta* **1975**, *12*, L27.