This assignment was subsequently confirmed by single-crystal X-ray analysis.[11] Interestingly, treatment of the corresponding phenol **9** under identical reaction conditions resulted in the production of epoxy alcohols **11** and **12** in approximately equal yield in addition to recovered **9** (26%).[9a,12] The structural assignment of **11** was also confirmed by single-crystal X-ray analysis.[11] *This result is of particular significance in that epoxy alcohol 11 possesses the correct connectivity and four of the five stereogenic centers present in SF 2315B (2).*[11]

Gaudiano and Koch have reported that the quinone methide of daunomycin reacts with molecular oxygen resulting in several products of oxidation.[13] On the basis of their work, and others,[14] the reaction mechanism we propose, outlined in Scheme III, accounts for the various products obtained upon treatment of quinones **6** and **9** with tetrabutylammonium fluoride. The initial step is loss of a proton from the C6 position of quinone **6** or **9**, resulting in generation of the corresponding quinone methide **13**. Subsequent electron transfer to molecular oxygen then produces semiquinone methide **14** which traps molecular oxygen to provide peroxy radical **15**.[15] One-electron transfer from quinone methide **13** to peroxy radical **15** then serves to produce peroxide **16** and generate additional semiquinone methide **14**. Intramolecular Michael addition of the peroxide group generates endoperoxide **17** and subsequent 1,3-elimination generates either epoxy alcohol **10** or **11** as the major product, depending upon the identity of the C8 substituent. In the case of acetate **17** (R = Ac), γ,δ-epoxide **10** is produced while phenol **17** (R = H) results in α,β-epoxide **11**. The observed difference in product distribution may be attributed to the generation of a dianionic species in the case of phenol **17**. Finally, we note reduction of the oxygen–oxygen bond at the stage of peroxide **16** accounts for production of carbinol **7**.

In summary, we have described an oxidation procedure which will find application in the total synthesis of SF 2315B. Currently, we are conducting labeling experiments to support our proposed mechanism and continue to direct our efforts toward the total synthesis of SF 2315B and related antibiotics.

Acknowledgment. This work was supported in part by the Welch Foundation (A-1230). G.A.S. thanks the American Cancer Society for a Junior Faculty Research Award. The R3m/V single-crystal X-ray diffractometer and crystallographic computing system in the Crystal and Molecular Structures Laboratory at the Department of Chemistry, Texas A&M University, was purchased from funds provided by the National Science Foundation (CHE-8513273).

Supplementary Material Available: Experimental procedures and spectral data for all compounds including the four-step conversion of **5** to **7** (6 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 form the ACS; see any current masthead page for ordering formation.

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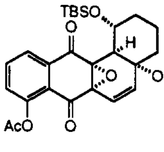
[10] A minor product (<10%), tentatively assigned the isomeric epoxy alcohol i, was also observed.



i

[11] The author has deposited atomic coordinates for this structure 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 1 EZ, UK.

[12] Since we have observed the isomerization of epoxy alcohol **11** to **12** during attempted recrystallizations, the actual kinetic product of this reaction may very well be **11** which isomerizes to **12** under the reaction conditions. The details of this rearrangement are currently under investigation and will be reported in a full account of this work.

[13] Gaudiano, G.; Koch, T. H. *J. Am. Chem. Soc.* **1990**, *112*, 9423.

[14] (a) Dowd, P.; Ham, S. W. *J. Am. Chem. Soc.* **1991**, *113*, 9403. (b) Lai, M.-T.; Liu, H.-W. *J. Am. Chem. Soc.* **1992**, *114*, 3160.

[15] In regard to the stereoselectivity of this process, examination of molecular models provides no evidence for a preferred steric approach of molecular oxygen to the α face of **13**. While we have no explanation for the observed stereoselectivity at this time, we note that epoxidation of the topologically similiar phenol **9** also occurs exclusively from the α face.

Synthesis and Reactivity of Enyne- and Dienyne-Tethered Molybdenum Carbene Complexes: Precursors to Polycyclic Frameworks

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Received July 1, 1992 (Revised Manuscript Received August 25, 1992)

Summary: Thermolysis of several enyne and dienyne tethered molybdenum–carbene complexes has been found to provide direct access to tricyclic ring systems.

Recently, studies from our group have demonstrated that the thermolysis of alkyne-tethered molybdenum carbene complexes in the presence of electron-poor olefins results in the formation of cyclopentenylcyclopropanes in good yield.[1] Work in our laboratories[2] and elsewhere[3] has shown that properly functionalized enynes will react with Fischer carbene complexes via a similar pathway to efficiently produce vinylcyclopropanes. Treatment of dienynes with Fischer carbene complexes has been demonstrated to smoothly produce hexahydroazulene systems via the [3,3]-sigmatropic rearrangement of *cis*-divinylcyclopropane intermediates.[4] All of these processes occur via the cyclopropanation of an alkene by an in situ generated vinylcarbene complex. Described herein are our initial investigations of the fully intramolecular version of this

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[1] (a) Harvey, D. F.; Brown, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 7806–7807. (b) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1991**, *32*, 5223–5226.

[2] (a) Harvey, D. F.; Lund, K. P.; Neil, D. A. *Tetrahedron Lett.* **1991**, *32*, 6311–6314. (b) Harvey, Lund, K. P.; Neil, D. A. *J. Am. Chem. Soc.*, in press.

[3] (a) Korkowski, P. F.; Hoye, T. R.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676–2678. (b) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070–2071. (c) Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 2841–2842.

[4] Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066–5068.

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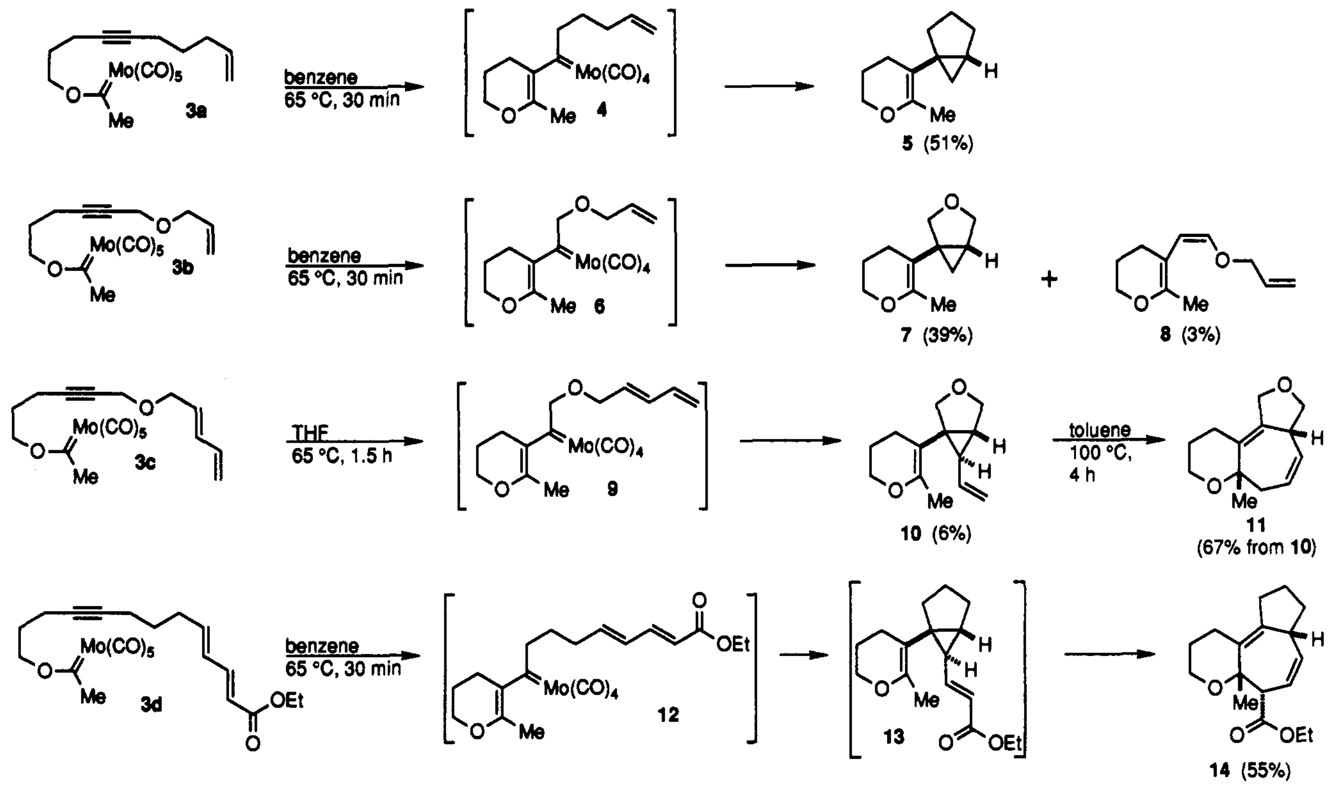
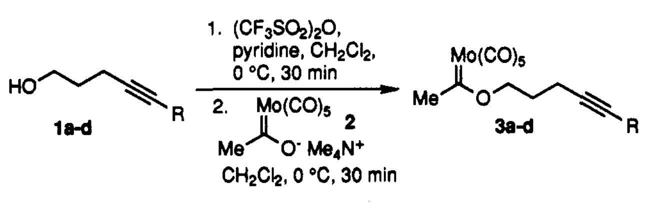


process in which an enyne or a dienyne is tethered to a molybdenum carbene complex. This process represents a rapid and direct method for the production of a variety of tricyclic frameworks.

Previous studies have demonstrated that oxygen-tethered carbene complexes can be prepared in excellent yield by the addition of primary alkyl triflates to the tetramethylammonium salt of molybdenum acylate complex **2**.[5] Alcohols **1a–d**[6] were treated with trifluoromethanesulfonic anhydride, using the procedure of Baum and coworkers,[7] to give the corresponding triflates in crude yields of 85–97%. Because of the high reactivity of these alkyl triflates, they were directly treated with molybdenum acylate **2**, followed by chromatography on silica gel, to give carbene complexes **3a–d** in 67–88% yield.[8] This procedure has been found to be general, as carbene complexes containing a variety of functional groups have been prepared via this protocol.[1b]



a R = $(CH_2)_3CH{=}CH_2$
b R = $CH_2OCH_2CH{=}CH_2$
c R = $CH_2OCH_2CH{=}CHCH{=}CH_2$
d R = $(CH_2)_3CH{=}CHCH{=}CHCO_2Et$

Thermolysis of complex **3a** at 65 °C for 1 h in benzene resulted in the formation of vinylcyclopropane **5** as the sole isolable product in 51% yield. The proposed mechanism for this process is analogous to those which have been suggested in previous studies.[1-4] Initial loss of CO, followed by reaction of the carbene center with the tethered alkyne produces vinylcarbene intermediate **4**. Intramolecular cyclopropanation of the tethered alkene then gives vinylcyclopropane **5**. The overall success of this cyclization with an unfunctionalized alkene was somewhat surprising since earlier studies had suggested that olefin activation or appropriate substitution on the tether between the alkyne and the alkene were required for this type of cyclization to be successful.[2] Hoye has reported a similar result for the thermolysis of an enyne tethered chromium methoxycarbene complex.[3a]

The presence of an allylic oxygen has been found to dramatically effect the reactivity of the olefin component of this three-component cyclization process.[2] The reactivity of molybdenum carbene complex **3b**, with an oxygenated tether between the alkyne and the alkene, was therefore investigated. Thermolysis of **3b** (benzene, 65 °C, 30 min) gave the desired vinylcyclopropane **7** in 39% yield. In addition, 1,3-diene **8** was obtained in 3% yield. The diene product is thought to arise via a 1,3-hydrogen shift from vinylcarbene complex **6**, followed by reductive elimination.[2b,9,10]

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(5) The tetramethylammonium salt **2** was prepared via Fischer's method and can be stored at −10 °C indefinitely with no noticeable decomposition. Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445–2456.

(6) Alcohols **1a–d** were prepared using standard synthetic procedures. Details are provided in the supplementary material.

(7) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* **1973**, *38*, 3673–3677.

(8) All new carbene complexes were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. All cyclization products were characterized by ^{1}H NMR, ^{13}C NMR, IR, LRMS, and HRMS or elemental analysis. Details are provided in the supplementary material.

(9) For related olefin formation pathways please see: (a) Fischer, E. O.; Maasböl, A. *J. Organomet. Chem.* **1968**, *12*, P15–P17. (b) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326–3331. (c) Casey, C. P.; Brunsvold, W. R. *Inorg. Chem.* **1977**, *16*, 391–396. (d) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726–6728. (e) Macomber, D. W. *Organometallics* **1984**, 1589–1591. (f) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Chem. Soc., Dalton Trans.* **1987**, 1041–1049. (g) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642–3659. (h) Lattuada, L.; Licandro, E.; Maiorana, S.; Papagni, A. *J. Chem. Soc., Chem. Commun.* **1991**, 437–438. (i) Söderberg, B. C.; Turbeville, M. J. *Organometallics* **1991**, *10*, 3951–3953. (j) Aoki, S.; Fujimura, T.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 2985–2990.

In order to extend this methodology to tricyclic fused-ring systems, two examples of dienyne-tethered molybdenum carbene complexes were investigated. Thermolysis (THF, 65 °C, 1.5 h) of **3c** gave the desired divinylcyclopropane **10**, but in only 6% yield. A variety of additional products were observed by TLC but could not be cleanly isolated or characterized. Thermolysis in benzene gave similar results. With this substrate it is anticipated that olefin metathesis and C–H insertion/reductive elimination pathways might compete with the desired cyclopropanation process.[2b] Cycloheptadiene **11**, resulting from the [3,3]-sigmatropic rearrangement of divinylcyclopropane **10**, was not observed during the thermolysis of carbene complex **3c** under the cyclization conditions described above.[11] However, thermolysis of divinylcyclopropane **10** at 100 °C for 4 h in toluene resulted in the smooth conversion of **10** to the tricyclic product **11** in 67% yield.[12]

Ester-substituted 1,3-dienes have been demonstrated to successfully undergo intramolecular cyclopropanation and rearrangement in related systems to give 1,4-cycloheptadienes in excellent yield.[2a] Indeed, thermolysis (65 °C, benzene, 2 h) of dienyne complex **3d**, containing an ester-activated 1,3-diene, gave the tricyclic product **14** in 55% yield as a single diastereomer. As in the previous systems, this product is believed to be produced via in situ generation of vinylcarbene complex **12** which subsequently cyclopropanates the 1,3-diene to give *cis*-divinylcyclopropane **13**. As has been observed in previous cases with donor–acceptor-substituted divinylcyclopropanes, divinylcyclopropane **11** is not isolated.[2a] The [3,3]-sigmatropic rearrangement of **13** smoothly occurs under the reaction conditions to give 1,4-cycloheptadiene **14**. The indicated stereochemistry for **11** and **14** is that expected to arise via the *cis*-divinylcyclopropane rearrangement occurring through a boat transition state.[11]

In summary, molybdenum carbene complexes containing tethered enyne and dienyne moieties have been prepared in excellent yield via the alkylation of the tetramethylammonium salt of molybdenum acylate complex **2**. Thermolysis of these systems leads to the formation of three rings in one step. The further development of this all-intramolecular molybdenum-mediated cyclization pathway, as well as its application to organic synthesis, is currently in progress.

Acknowledgment. Support from the Cancer Research Coordinating Committee of the University of California, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the American Cancer Society (Junior Faculty Research Award to D.F.H.), and the National Institutes of Health (GM41984) is gratefully acknowledged. The 500-MHz NMR spectrometer was purchased with assistance from the NIH (RR04733) and NSF (CHE 8814866).

Supplementary Material Available: Experimental procedures and compound characterization data (12 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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[10] The enol ether stereochemistry of 8 was assigned based on comparison of ^1H NMR spectra with 1,4-dialkoxy-1,3-butadienes prepared in a related fashion (Harvey, D. F.; Neil, D. A., manuscript in preparation).

[11] As determined by TLC comparison versus an authentic sample of 11.

[12] The [3,3] sigmatropic rearrangement is thought to occur via a boat transition state. See: Piers, E.; Morton, G. E.; Nagakura, I.; Thies, R. W. *Can. J. Chem.* **1983**, *61*, 1226–1238 and references cited therein.

Electrochemically Promoted Cyclocoupling of 1,3-Dienes or Styrenes with Aliphatic Carboxylic Esters[1]

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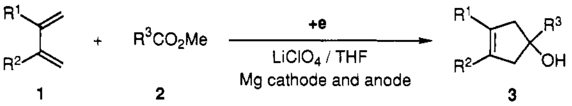
Received May 19, 1992

Summary: The cathodic cyclocoupling of 1,3-dienes **1** with aliphatic esters **2** is promoted by a magnesium electrode and yields homologs of 3-cyclopentenol. Under similar reaction conditions, the coupling of styrenes with **2** affords 2-phenylcyclopropanol derivatives, and this coupling reaction has been successfully applied to the synthesis of *ar*-dihydroturmerone and curcumone.

It is well-known that a 6-membered ring is easily formed by the [2 + 4] cycloaddition of a 1,3-diene **1** with a suitable dienophile, whereas formation of a 5-membered ring from a 1,3-diene is not always straightforward.[2,3]

Scheme I



However, it has been found in the present study that the electroreduction of a solution of **1** and an aliphatic carboxylic ester **2** with a magnesium electrode[4] gives a 3-cyclopentenol type of compound **3** in one step (Scheme I). This novel electroreductive cyclocoupling is the equivalent of a 1,4-addition of a one-carbon unit to **1**[7] and represents one of the simplest methods of formation of a 5-membered ring system from **1**.

The use of Mg as the electrode was one of the most important factors in the formation of **3**, since the elec-

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[1] Electroorganic Chemistry. 138. For part 137: Regioselective Synthesis of Substituted Tropones and Azulenes using Anodic Oxidation of Cycloheptatriene Systems as the Key Reaction. Shono, T.; Okada, T.; Furuse, T.; Kashimura, S.; Nozoe, T.; Maekawa, H. *Tetrahedron Lett.*, in press.

[2] Corey, E. J.; Walinsky, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 8932.

[3] Danheiser, R. L.; Martinez-Davila, C.; Auchus, R. J.; Kadonaga, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 2443 and references cited therein.

[4] We have recently found that the Mg electrode promotes a variety of unique reactions such as cathodic coupling of chlorosilanes yielding polysilane[5] and electroreduction of aliphatic esters.[6]

[5] Shono, T.; Kashimura, S.; Ishifune, M.; Nishida, R. *J. Chem. Soc., Chem. Commun.* **1990**, *17*, 1160.

[6] Shono, T.; Masuda, H.; Murase, H.; Shimomura, M.; Kashimura, S. *J. Org. Chem.* **1992**, *57*, 1061.

[7] Erker, G.; Engel, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 3311.