angle = 12.8°) and the W, O(1), C(1), and C(2) atoms are coplanar to within 0.001 Å, it is roughly perpendicular to the P–W vector (angle between the W–acrolein and P–N–C(13)–O(1)–W least-squares planes = 70.1°) and it is present in the s-trans conformation as would be expected on the basis of a recent theoretical study.[22] The acrolein C–C and C–O bond lengths are similar to those seen in other structures of Lewis acid adducts of α,β-unsaturated enones,[23] while the tungsten–oxygen bond length is relatively long,[18a,24] which is in accord with the catalytic activity of 1.

In conclusion, a novel transition-metal catalyst for the Diels–Alder reaction has been discovered. On the basis of a rare X-ray crystal structure of a Lewis acid–dienophile adduct, it is reasonable to suggest that the catalytic activity of 1 is due solely to its Lewis acidity. While the catalyst described here is achiral, chiral analogues may be envisioned readily. Chiral catalysis of the *hetero*-Diels–Alder reaction—which is not observed for acrolein here—is known,[25a–c] as is chiral Diels–Alder induction by stoichiometric amounts of chiral Lewis acids,[25d,e] but true Diels–Alder *catalysis* with high asymmetric induction remains unknown.[16,25] Work is in progress on the design and synthesis of such a catalyst.

Acknowledgment. We thank Professor M. E. Jung for several helpful discussions. Financial support from the UCLA Committee on Research, a Biomedical Research Support Grant, and Merck & Co. is gratefully acknowledged.

Supplementary Material Available: Characterization of 3 and 4 and tables of crystallographic data for 4 and details of the solution (15 pages). Ordering information is given on any current masthead page.

Robert V. Honeychuck, Peter V. Bonnesen
Judah Farahi, William H. Hersh*
Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

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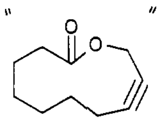
Preparation of Medium-Ring Acetylenic Lactones Utilizing Metal-Promoted Alkyne Bending

Summary: Reaction of a variety of acetylenic hydroxycarbonyl compounds with $Co_2(CO)_8$ gives rise to readily isolated alkyne–$Co_2(CO)_6$ complexes in which lactonization, previously impossible due to geometric constraints, proceeds relatively smoothly due to "bending" of the alkyne moiety upon metal coordination.

Sir: In connection with ongoing studies of intramolecular Pauson-Khand-type cyclization reactions,[1,2] we required access to 11-membered ring acetylenic lactones, e.g., 1.[3]



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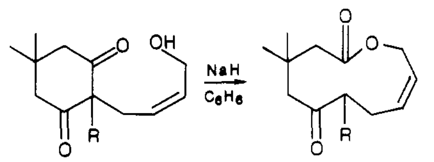
Four reports of 12-membered ring lactones containing triple bonds may be found in the literature.[4] In two cases, favorable conformational effects allow intramolecular oxygen bridging to occur leading to "highly strained" compounds with the triple bond in a 10-membered ether–lactone ring.[4a,c] Considering odd-size rings, the smallest lactone containing triple bonds is a 15-membered ether–lactone.[5]

A simple entry into 11-membered ring lactones (without a triple bond, of course), developed by Mahajan,[6] utilizes an intramolecular retro-Dieckmann reaction (eq 1). Direct



(1)

application to an acetylenic analogue is geometrically impossible due to the linear nature of the butynyl unit. However, metal complexation of alkynes by reaction with $Co_2(CO)_8$ results in a substantial geometric change to a system with ca. 140° bond angles about the "alkyne" carbons.[7] It therefore seemed entirely reasonable that precomplexation with $Co_2(CO)_8$ would result in a system capable of the desired lactonization, provided that the complexed alkyne function survived the conditions required for the process.[8]

Several substrates for investigation were prepared by alkylation of cyclic ketones with $BrCH_2C{\equiv}CCH_2OSi$-*t*-$BuMe_2$[9] (Table I). Desilylation followed by reaction with

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[6] Mahajan, J. R. *Synthesis* **1976**, 110.

[7] Dickson, R. S.; Fraser, P. J. *Adv. Organomet.* Chem. **1974**, *12*, 323.

[8] While this work was in progress, Schreiber and co-workers reported a similar use of alkyne complexation to form metal-complexed medium-ring acetylenic carbocycles via low-temperature alkylations.[2g]

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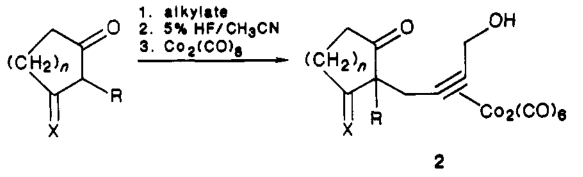
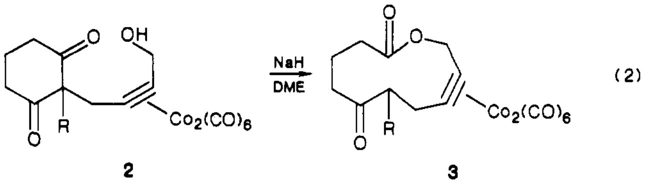
Table I. Preparation of Complexed Alkynyl Ketones 2



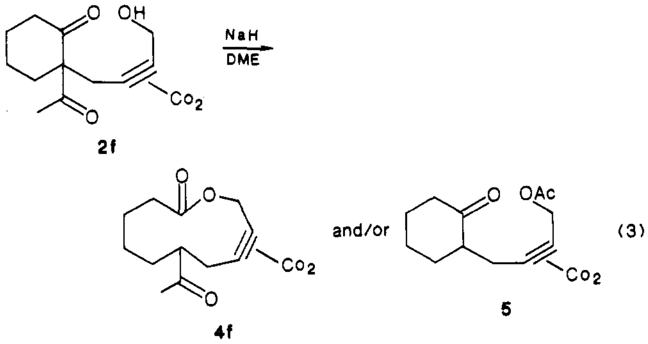
compound	alkylation conditions	yield, % alkylation	desilylation	complexation
a, $n = 1$, R = CH_3, X = O	NaH, DMF, 25 °C, 15 h	30	90	50
b, $n = 2$, R = CH_3, X = O	NaH, DMF, 25 °C, 15 h	56	86	47
c, $n = 2$, R = $CH_2CH{=}CH_2$, X = O	KOEt, EtOH, 78 °C, 8 h	57	91	53
d, $n = 2$, R = CO_2Et, X = H_2	NaH, DMF, 25 °C, 15 h	100	99	52
e, $n = 2$, R = SO_2Ph, X = H_2	NaH, DMF, 25 °C, 16 h	58	98	72
f, $n = 2$, R = $COCH_3$, X = H_2	NaH, DMF, 25 °C, 15 h	95	95	75

$Co_2(CO)_8$ gave the protected alkynyl ketones **2** in generally satisfactory yields.[10] Having six potential substrates on hand, we investigated a variety of conditions for lactonization using the Mahajan system as a model. Treatment of **2b** under these conditions (catalytic NaH, benzene, reflux 6 h) led to decomposition. However, reaction with 1 equiv of NaH in 1,2-dimethoxyethane at *room temperature* overnight led to cobalt-complexed lactone **3b** in 71% isolated yield.[11] The product **3b** was readily identified by IR and NMR (^1H and ^{13}C), showing in the latter characteristic signals for the diastereotopic protons on both propargyl carbons.[12] The allylic analogue **2c** undergoes much the same transformation, yielding complexed acetylenic lactone **3c** in 50% yield under the same conditions (eq 2). Most encouraging for the application of the products of these reactions in conventional reaction chemistry is the observation that oxidative removal of the cobalt from **3b** gives rise to the uncomplexed lactone as a white, crystalline solid,[13] which upon re-treatment with $Co_2(CO)_8$ returns **3b** in quantitative yield. *Thus for practical purposes acetylenic lactones of this ring size may be considered to be stable, isolable, synthetically usable species.*



b, R = methyl
c, R = allyl

Extension of this methodology to either keto ester **2d** or keto sulfone **2e** has been unsuccessful. In each case the corresponding alkoxide shows no tendency to cyclize at 45 °C, with higher temperatures leading to decomposition. In the case of diketone **2f**, the interesting possibility of addition to either of two distinct carbonyl groups was present. Reaction at the cyclohexanone carbonyl would lead to the desired lactone **4f**, while attack at the acetyl moiety would give rise to acetate **5** (eq 3).



Reaction of **2f** with NaH turns out to be very slow, even at 40 °C; after 1 week a 21% yield of **5** is obtained as the only product, together with about an equal amount of unreacted starting material. Assuming that the preferred conformation of **2f** places the complexed butynyl side chain equatorial, attack of the alkoxide on either face of the cyclohexanone carbonyl faces interference from an axial group (H on the face cis to the side chain and acetyl on the face trans to it). The alternative reaction at the acetyl carbonyl faces no such encumbrance and may proceed through a relatively strain-free 4-cycloheptene-like chair transition state. This explanation readily rationalizes the ease of reaction of systems **2b** and **2c**: the second ring carbonyl eliminates the interfering axial hydrogen.

Work aimed at testing the applicability of this approach to smaller rings has begun. Cyclopentanedione derivative **2a** was prepared (Table I) but was found to be unreactive in all attempts to prepare the 10-membered analogue of **3b**. We were, however, successful in applying a more conventional lactonization process to the synthesis of a 10-membered ring acetylenic lactone. Thus, cyclization of cobalt-complexed hydroxy acid **6**[14] using the Mukaiyama procedure[15] does proceed in spite of the extended reflux required, affording 22% of lactone **7**[16] together with 15% of the corresponding 20-membered ring compound.

Finally, and most remarkably, the analogous cyclization of complexed acid **8** proceeds in a similar manner to give 28% isolated, purified yield of **9**,[16] a cobalt-complexed *seven-membered ring* acetylenic lactone. In both the

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[9] Prepared from 1,4-butynediol by monoprotection (0.12 equiv of TBDMSCl, imidazole, DMF, 35 °C, 18 h, 93%) and bromination (CBr_4, PPh_3, Et_2O, 25 °C, 4 h, 90%).

[10] Desilylation conditions: 5% aqueous HF in CH_3CN, 25 °C, 1 h. Complexation: 1.1 equiv of $Co_2(CO)_8$ in ether, 25 °C, 4 h. Isolated yields: all compounds characterized by spectroscopic and/or elemental analysis (see supplementary material).

[11] Indeed, a sample of **2b** stored neat at 0 °C for 2 weeks was found to have undergone *spontaneous* lactonization in the complete absence of base!

[12] Partial ^1H NMR (300 MHz, C_6D_6) δ 2.47 (br d, J = 12 Hz, 1 H), 3.42 (t, J = 12 Hz, 1 H), 4.65 (d, J = 15 Hz, 1 H), 5.46 (d, J = 15 Hz, 1 H).

[13] Partial ^1H NMR δ 4.55 (ddd, J = 1.5, 2.5, 15 Hz, 1 H), 4.65 (dt, J_d = 15 Hz, J_t = 2.5 Hz, 1 H).

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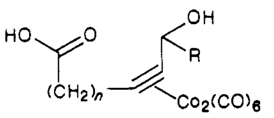
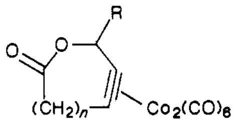
[16] For **7**: partial ^1H NMR δ 5.11 (s, 2 H); mol wt (isopiestic) calcd 438, found, 448 ± 25. For **9**: partial ^1H NMR δ 4.44 (d, J = 8.1 Hz, 1 H).

preparations of **7** and **9** considerable cobalt salt formation is observed as well, presumably via oxidation by the chloropyridinium reagent. It therefore may well be possible to improve these lactonizations by making use of alternative procedures that avoid this type of reagent. Our goal in this study has nonetheless been amply realized. Given the importance of medium-ring lactones in natural products chemistry and the versatility of the carbon–carbon triple bond in synthesis, the accessibility of these systems gives rise to intriguing new possibilities in both areas. Furthermore, it is clear that the utility of the cobalt–alkyne functional group in relatively complex synthetic situations is quite considerable, especially in terms of tolerance to a variety of reaction conditions. Certainly the ability to reversibly "bend" an alkyne in order to render feasible otherwise geometrically impossible transformations should be of considerable general utility, and we hope to report on additional experiments along these lines in the near future.



6, $n = 5$; R = H
7, $n = 2$; R = $CH(CH_3)_2$



7, $n = 5$; R = H
9, $n = 2$; R = $CH(CH_3)_2$

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Supplementary Material Available: Analytical and/or spectroscopic data for all compounds (6 pages). Ordering information is given on any current masthead page.

Neil E. Schore,* Samir D. Najdi
Department of Chemistry
University of California, Davis
Davis, California 95616

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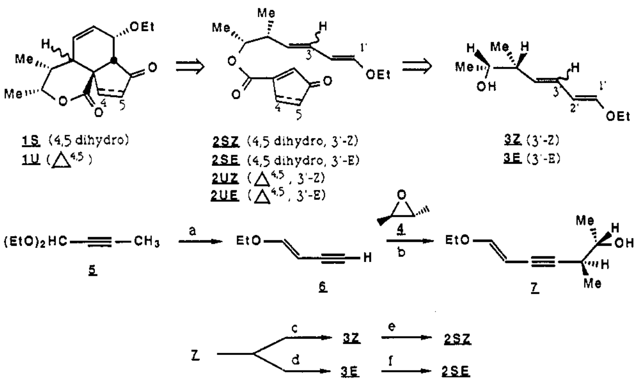
Efficient Generation and Use of 3-Carboalkoxycyclopentadienone as a Diels–Alder Dienophile[1]

Summary: Treatment of benzyl 4-oxo-1-(phenylsulfonyl)cyclopent-2-ene-1-carboxylate (**11**) with amine base provides in situ generation of the cyclopentadienone moiety which has been shown to react with various dienes. Reaction temperature decreases up to 100 °C were noted for these activated substrates by comparison to the corresponding "nonactivated" 3-carboalkoxycyclopentenone cycloadditions.

Sir: In conjunction with our synthetic program we wished to effect the synthesis of tricyclic lactone **1S** via intramolecular Diels–Alder reaction of dienes **2SZ** or **2SE**. Of greatest interest was (*Z*)-diene **2SZ** since it offered the potential of using the chirality at the pentadienylic 5′-position to dictate selection of the proper diastereotopic face of the cyclopentenone moiety.[2] Moreover, since both of the dienyl ether fragments (**3Z** and **3E**) are prepared from acetylide addition to *trans*-butene oxide (see Scheme I[3]), utilization of the corresponding chiral epoxide would ultimately provide access to the optically active tricyclic intermediate **1S**.

Scheme I[a]



[a] (a) Lithium aminopropylamide, −35 °C, 8 h (79%; 4:1, *E*/*Z*); (b) toluene, (i) *n*-BuLi, −78 °C, (ii) Me_3Al, 0 °C, (iii) **4**, 40°C (72%); (c) benzene, $Pd/CaCO_3$, H_2 (95%); (d) THF, LAH, reflux 8 h (78%); (e) 3-oxocyclopent-1-ene-1-carboxylic acid, CH_2Cl_2, diisopropylcarbodiimide, DMAP, 1 h (81%); (f) same as e (83%).

Unfortunately, both **2SZ** and **2SE** are inert to thermolysis as dilute solutions at temperatures of 200 °C for 24 h. Higher temperatures serve only to consume starting material without concomitant production of any Diels–Alder products. In considering ways to activate the dienophile moiety we became intrigued with the possibility of using 3-carboalkoxycyclopentadienones **2UZ** and **2UE** as the locus for the intramolecular Diels–Alder reaction.

Although Diels–Alder chemistry of cyclopentadienone itself is well-known,[4] its efficient use as a dienophile is hampered by the competitive dimerization process.[5] Furthermore, 3-carboalkoxy-substituted cyclopentadienones have only been reported for special cases bearing three additional aryl or tert-butyl groups.[6] Therefore, prior to investigating the chemistry of **2UZ** and **2UE** we deemed it prudent to first investigate the *intermolecular* Diels–Alder reactions of 3-carboalkoxycyclopentadienone.

Synthetic access to the various 3-substituted cyclopentadienones proved to be highly efficient by the method shown in Scheme II.[3] Oxidation of α-sulfonyl ester **8**[7] with MCPBA affords epoxide **9** as a single diastereomer in 89% yield. Conversion of **9** to allyl alcohol **10** is smoothly accomplished by minor modification of the method of Noyori.[8] Manganese dioxide[9] oxidation of the allyl alcohol **10** provides enone **11**, the progenitor of 3-carbobenzoxy-

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[1] Bruceantin support studies 13. For paper 12, see: Kuo, F.; Fuchs, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 1122.

[2] For leading references dealing with the use of (*Z*)-dienes in intramolecular Diels–Alder reactions, see: Palmer, J. T.; Learn, K. S.; Fuchs, P. L. *Synth. Commun.* **1986**, *16*, 1315.

[3] Experimental details for the prepartion of compounds **2SZ, 2SE, 2UZ, 2UE, 4–12, 13Z, 13E, 14,** and **16–19** can be found in the supplementary material.

[4] a) Review: Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261. (b) DePuy, C. H.; Isaks, M.; Eilers, K. L. *J. Org. Chem.* **1964**, *29*, 3503. (c) DePuy, C. H.; Lyons, C. E. *J. Am. Chem. Soc.* **1960**, *82*, 631. (d) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 962.

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