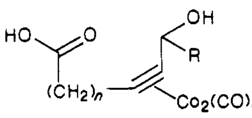
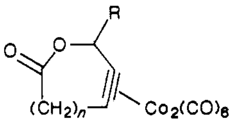
preparations of 7 and 9 considerable cobalt salt formation is observed as well, presumably via oxidation by the chloropyridinium reagent. It therefore may well be possible to improve these lactonizations by making use of alternative procedures that avoid this type of reagent. Our goal in this study has 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 = $CH(CH_3)_2$

Acknowledgment. We thank the National Institutes of Health (Grant GM 26294) for financial support of this research.

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

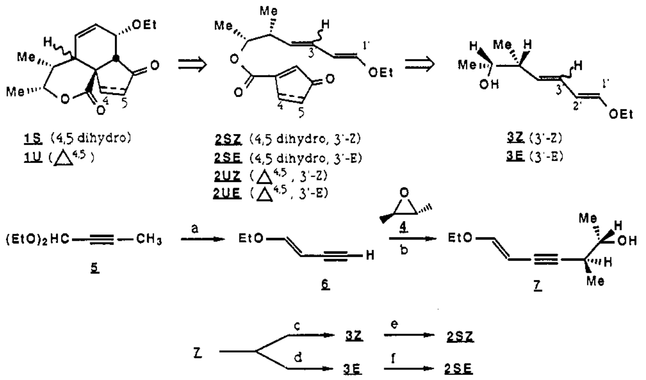
Neil E. Schore,* Samir D. Najdi
Department of Chemistry
University of California, Davis
Davis, California 95616
Received September 4, 1987

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.

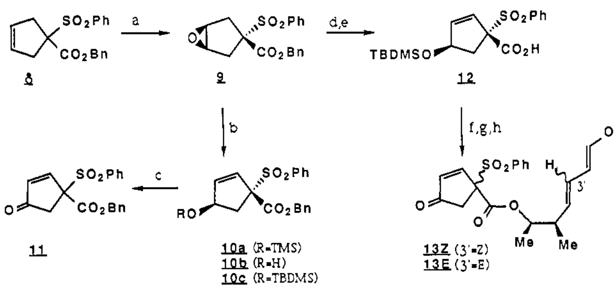
(3) Experimental details for the prepartion of compounds **2SZ**, **2SE**, **2UZ**, **2UE**, **4–12**, **13Z**, **13E**, **14**, and **16–19** can be found in the supplementary material.

(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.

(5) The use of cyclopentadienone as a dienophile is best exemplified by the "three-phase" polymer work of Gaviña. (a) Gaviña, F.; Costero, A. M.; Gil, P. B.; Luis, S. V. *J. Am. Chem. Soc.* 1981, *103*, 1797; (b) **1984**, *106*, 2077.

(6) Ried, W.; Kinkel, W.; Olschewski, P. B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 275.

Scheme II[a]

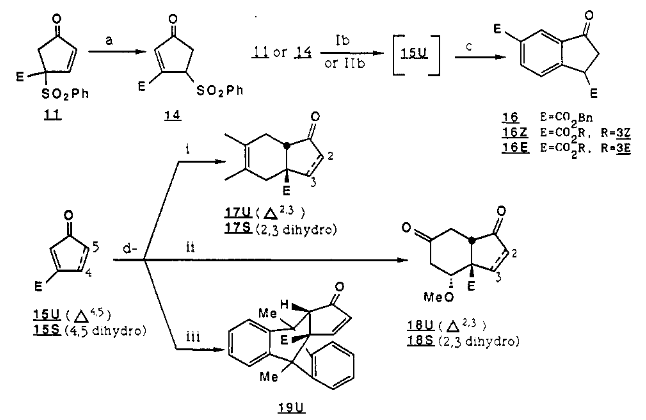


[a] (a) MCPBA, CH_2Cl_2, 0 °C (90%); (b) (i) TMSOTf, diisopropylethylamine, DBU, benzene, room temperature 5 h to **10a**, (ii) 5% HCl, 0 °C, 0.5 h to **10b** (95% i + ii); (c) MnO, CH_2Cl_2, room temperature 12 h (91%); (d) step b i, using TBDMSOTf (97%); (e) 10% Pd/C, EtOH, 1,4-cyclohexadiene (90%); (f) dienyl alcohol **3Z** or **3E**, DCC, CH_2Cl_2 (60–84%); (g) $(n\text{-}Bu)_4NF$, THF, 0 °C (91%); (h) (i) TFAA, DMSO, CH_2Cl_2, −78 °C, (ii) Et_3N (75%).

cyclopentadienone. Alternatively, conversion of allylic silyl ether **12** to **13Z** and **13E** (precursors of **2UZ** and **2UE**, respectively) was accomplished by esterification with the corresponding alcohol followed by silyl group removal and oxidation.

As a prelude to base-catalyzed eliminations, the γ-sulfonyl enone **11** was heated in toluene at 145 °C in a sealed tube in the absence of base for 8 h to afford the rearranged sulfone **14** in nearly quantitative yield. Presumably this transformation involves the enol of **11** as an intermediate which undergoes a [1,5]-sigmatropic shift[10] of the sulfonyl moiety.[11] Although both **11** and **14** are able to serve as precursors of 3-carbobenzoxycyclopentadienone (**15**), it has been consistently observed that yields of the Diels–Alder adducts are 15–20% higher when employing **11**. Generation of **15U** by slow addition of **11** (or **14**) to a solution of tripropylamine in toluene at reflux (in the absence of any added diene) affords dimer **16**[12] in 75% (52% from **14**) yield. Repetition of this base-catalyzed protocol in the presence of excess 2,3-dimethyl-1,3-butadiene, 2-[(trimethylsilyl)oxy]-4-methoxy-1,3-butadiene,[13] or 9,10-dimethylanthracene[14] affords Diels–Alder adducts **17–19**, respectively. An indication of the activation afforded by the second double bond in **15U** is seen by comparing the reaction of 3-(benzyloxycarbonyl)cyclopentenone **15S** with 2,3-dimethyl-1,3-butadiene and 2-[(trimethylsilyl)oxy]-4-methoxy-1,3-butadiene. As can be seen in the Scheme III, more extended reaction times and temperatures over 100 °C higher were required to effect the Diels–Alder reactions leading to adducts **17S** and **18S** respectively.

Scheme III[a]



[a] E = CO_2Bn unless otherwise defined; U represents the reaction employing **15U**, whereas S represents the reaction employing **15S**: (a) toluene (sealed tube), 145 °C, 8 h (96%), (b) (I) from **11**, (II) from **14**; Et_3N or Pr_3N, 50 °C; (c) Pr_3N, toluene, reflux [(I) 75%, (II) 52%]; (d) (i) 2,3-dimethyl-1,3-butadiene (5 equiv); U, Pr_3N, benzene, 50 °C, 20 h [(I) 84%, (II) 71%]; S; toluene (sealed tube), 155 °C, 24 h (89%); (ii) 1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene (5 equiv); U, Pr_3N, benzene, 50 °C, 20 h [(I) 89%, (II) 71%]; S, toluene (sealed tube), 140 °C, 24 h (34%); (iii) 9,10-dimethylanthracene (1.5 equiv), Pr_3N, toluene, reflux 4 h [(I) 36% **19U** and 16% **16**].

Unfortunately, attempts to extend these successes to the intramolecular cases were uniformly unsuccessful. Slow addition of either **13Z** or **13E** to a solution of amine base in various solvents at temperatures ranging between 100 and 180 °C failed to afford Diels–Alder adduct **1U** or any regioisomer thereof. Dienone intermediates **2UZ** and **2UE** eschew the opportunity to undergo the intramolecular reaction and only produce the dimeric adducts **16Z** and **16E**, each as mixture of diastereomers.

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Supplementary Material Available: Experimental details and ^1H NMR spectral and analytical data (21 pages). Ordering information is given on any current masthead page.

M. H. Nantz, P. L. Fuchs*
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Received August 12, 1987

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(7) Nantz, M. H.; Radisson, X.; Fuchs, P. L. *Synth. Commun.* **1987**, *17*, 55.

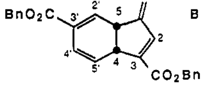
(8) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 2738.

(9) Fatiadi, A. J. *Synthesis* **1976**, 65.

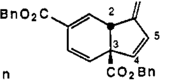
(10) For leading references on similar 1,5-sigmatropic rearrangements in cyclopentadienyl systems, see: Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187.

(11) An alternative mechanism involving readdition of benzenesulfinic acid to **15** appears less likely since addition of 2,3-dimethylbutadiene to this mixture does not afford adduct **17**.

(12) The formation of **16** formally appears to result from addition of the C4,5 olefin to a molecule of **15** serving as an electron-deficient diene, followed by carbon monoxide extrusion (to yield i) and aromatization.



(i)



(ii)

However, a plausible alternative involves addition of the C2,3 olefin, ultimately generating ii, an intermediate that could directly provide **16a** via 1,9-sigmatropic migration via its enolic form.

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