Journal of Organometallic Chemistry, 431 (1992) 335–358
Elsevier Sequoia S.A., Lausanne
JOM 22552

Use of metal complexation in the synthesis of medium-ring acetylenic lactones

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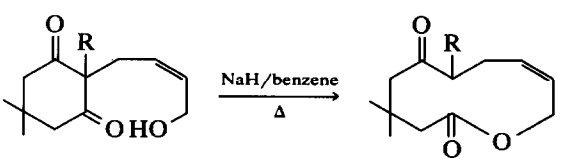
(Received September 24, 1991; in revised form November 25, 1991)

Abstract

The hexacarbonyldicobalt complexes of several appropriately designed acetylenic lactone precursors have been prepared, and lactones containing $Co_2(CO)_6$-complexed triple bonds in seven-, ten-, and eleven-membered rings obtained. The latter were best obtained through a retro-Dieckmann fragmentation of 2-(hydroxybutynyl) derivatives of 1,3-cyclohexanedione. Attempts to extend this reaction to cyclohexanones bearing other anion-stabilizing groups in the 2-position or to 1,3-cyclopentanediones were unsuccessful. Decomplexation afforded the metal-free 11-ring lactone, characterized crystallographically. Treatment of this system with basic reagents led to dimerization. In the case of the smaller rings, cyclization of the complexed acetylenic hydroxyacids under Mukaiyama conditions (2-chloro-*N*-methylpyridinium iodide, CH_2Cl_2, reflux) succeeded in modest yields.

Introduction

The chemistry of macrocyclic lactones has attracted considerable attention [1]. Such systems are generated by cyclization of open chain precursors or by cleavage of internal bonds in polycyclic systems [2]. In 1976 Mahajan [3] reported the base-induced retro-Dieckmann fragmentation of 2,2-dialkylcycloalkane-1,3-diones (**1**) to give 11-membered ring lactones (**2**) in good yield (eq. 1).



(1)

(**1**, R = Me, Allyl) (**2**)

Several groups have reported [4,5] the preparation of medium-ring lactones by means of base catalyzed fragmentation of lactols with an electron-withdrawing

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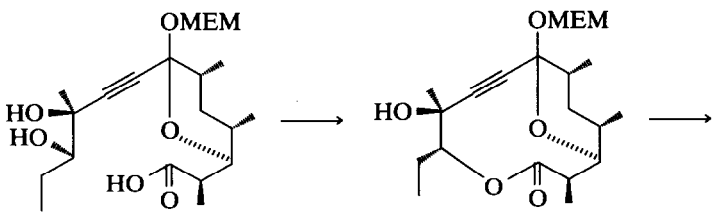
group at an angular carbon. Suginome and Yamada [6] prepared a number of medium-ring (9- to 11-membered) lactones by a regioselective β-scission of alkoxy radicals. However, the literature contains only a few reports [7] in which medium-ring acetylenic lactones have been synthesized. In two cases ring closure was facilitated by oxygen bridging (*e.g.* in **3**) permitting formation of highly strained compounds [8a,8b] such as **4**. The 10-membered ring oxygen bridged-acetylenic lactone was transformed ultimately to the 12-membered ring macrolide methynolide **5** [8a] (eq. 2).



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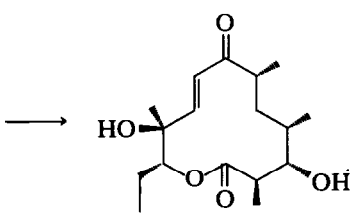
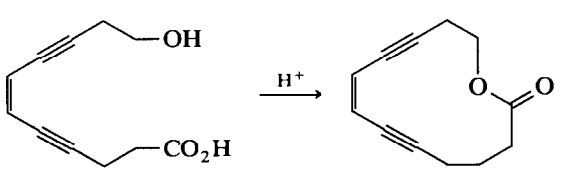


(5) (2)

In another case, the rigidity of the acyclic precursor, the (*Z*)-ene-diyne hydroxy acid **6** (eq. 3), enabled intramolecular lactonization to the 13-membered ring system **7** to compete with intermolecular esterification [8c].

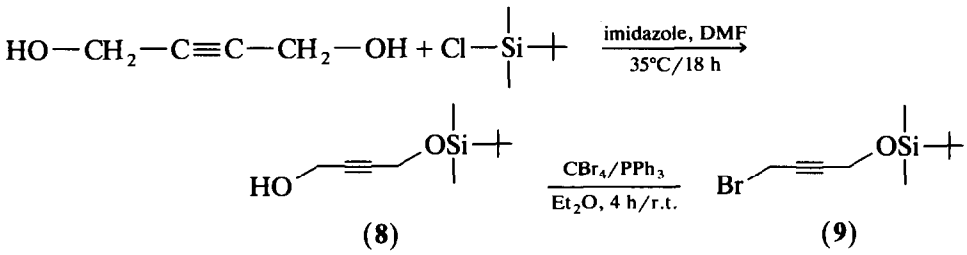


(6) (7) (3)

Results and discussion

11-membered ring acetylenic lactones

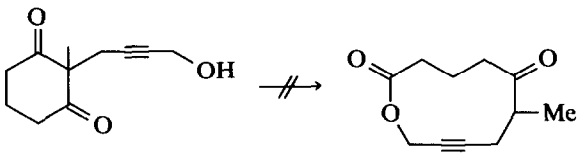
As an initial target for study we chose an 11-membered ring system. Direct application of the Mahajan procedure to an acetylenic analog was of course not expected to succeed due to the linear nature of the side chain. However, complexation of an alkyne by reaction with octacarbonyldicobalt leads to a substantial geometric change, where the RCCR′ moiety in the $(RCCR')Co_2(CO)_6$ complex is bent to a *ca.* 140° bond angle [9]. Therefore, pre-complexation of the butynyl unit with $Co_2(CO)_8$ was expected to result in a system capable of the desired lactonization. This section describes the synthesis of a variety of cyclic ketone complexes



(8) (9)

Scheme 1.

necessary to demonstrate the scope and limitations of this modification of intramolecular retro-Dieckmann lactonization.

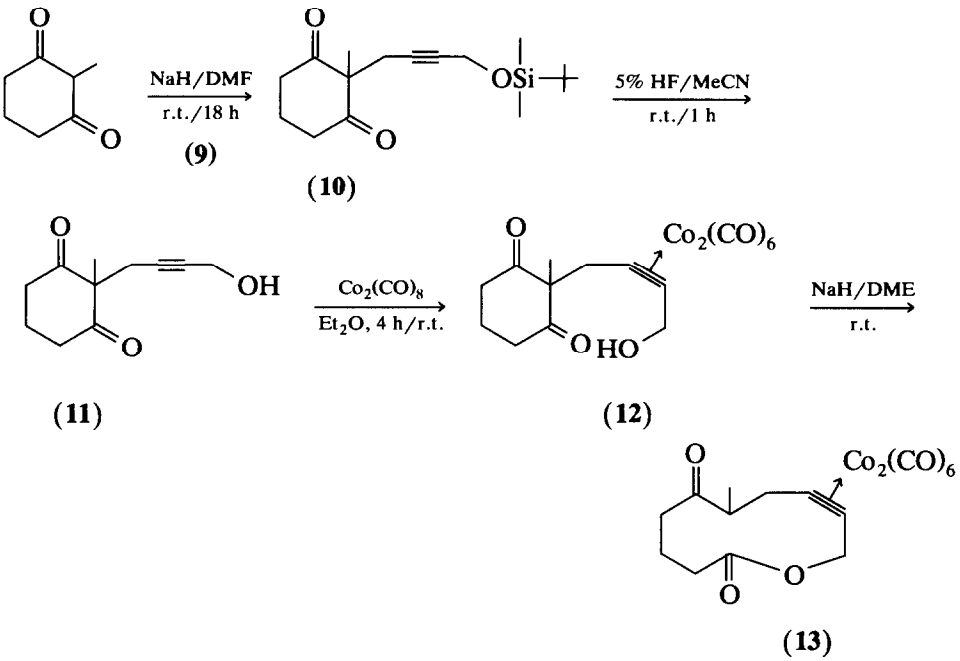


The hydroxybutynyl dione complex **12** was prepared by a sequence of alkylation, alcohol deprotection, and finally complexation with $Co_2(CO)_8$. Alkylating agent **9** was prepared in 85% overall yield (Scheme 1) by monosilylation of 2-butyne-1,4-diol with 0.12 equivalents of t-butyldimethylsilyl chloride [10] to give **8**, followed by bromination [11].

Attempts to alkylate 2-methyl-1,3-cyclohexanedione with **9** employing ^{t}BuOK in ^{t}BuOH [3,12], lithium diisopropylamide (LDA) in tetrahydrofuran (THF), KOH in diglyme [13], NaH in THF, or KOH in methanol [14] were unsuccessful. However, NaH in DMF at room temperature [15] gave **10** in 56% yield (Scheme 2). The ^{1}H-NMR spectrum of **10** showed the expected triplets at 2.63 and 4.19 ppm ($J = 2.1$ Hz) for the coupled sets of propargyl methylene protons, consistent with C– and not O–alkylation. Deprotection with 5% HF in acetonitrile [16] gave the hydroxybutynyl dione **11** in 87% yield. Reaction of **11** with 10% excess of $Co_2(CO)_8$ in ether gave air-stable dark red crystals of the complexed alkynyl dione **12** in 57% yield. The ^{1}H-NMR (C_6D_6) of this compound showed a methylene doublet ($J = 6$ Hz) at 4.45 ppm due to coupling with the OH proton. Complexation eliminated the long range coupling between the two propargyl methylenes. In the ^{13}C-NMR spectrum the carbons of the complexed alkyne were shifted downfield to 92 and 98 ppm.

Refluxing a benzene solution of **12** with catalytic NaH led to decomposition. Repetition in C_6D_6 at 25°C showed (^{1}H-NMR) that the complexed lactone was formed, but the reaction took 8 days. Repeating with one equivalent of NaH in 1,2-dimethoxyethane (DME) at 25°C overnight led to complexed lactone **13** in 71% isolated yield.

The product was readily identified spectroscopically, the IR showing ketone and lactone peaks at 1718 and 1745 cm^{-1}, respectively. Both propargyl methylenes were diastereotopic by NMR. The CH_2O protons were split into two doublets at 5.38 and at 4.58 ppm with $J = 13$ Hz, whereas the other propargyl methylene protons CH_2C were split into a doublet of doublets at 3.36 ppm ($J = 15.1$, 11.6 Hz)

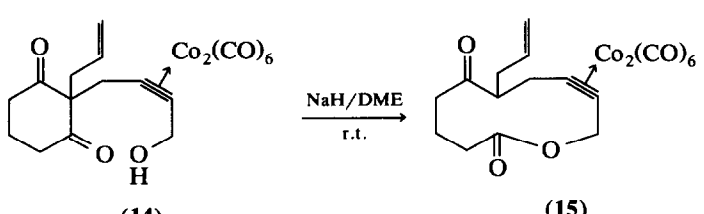


Scheme 2.

and a broad doublet at 2.41 ppm ($J = 15.1$ Hz). The methyl group showed a doublet at 0.63 ppm. In the ^{13}C-NMR spectrum a signal for the lactone carbonyl carbon was observed at 171 ppm.

Several analogs were prepared. Alkylation of 2-allyl-1,3-cyclohexanedione [17,18] with **9** using sodium ethoxide in refluxing ethanol gave the best results. Desilylation followed by $Co_2(CO)_8$ complexation produced complex **14** as a red viscous oil in a good yield, again air and thermally stable at room temperature.

Stirring **14** with NaH in DME gave complexed acetylenic lactone **15** in 50% isolated yield (eq. 4).

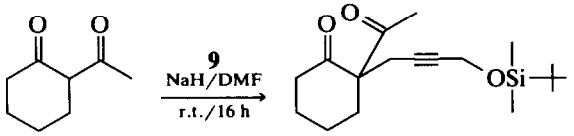


(14) (15) (4)

The structure of the lactone was again established spectroscopically. The lactone carbonyl band appeared at 1747 cm^{-1} in the IR and two sets of diastereotopic propargyl methylene groups were seen by ^{1}H-NMR.

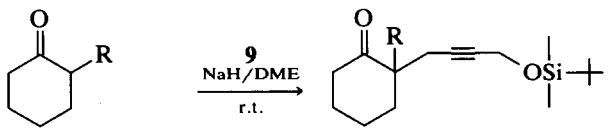
Attempting to extend this methodology to cyclic ketones containing other electron-withdrawing functionalities, 2-acetylcyclohexanone was added to NaH in DMF followed by addition of **9**, giving the ketone **16** in 95% isolated yield (eq. 5). 2-Phenylsulfonecyclohexanone (**17**) [19,20] and 2-carboethoxycyclohexanone (**18**)

were alkylated with **9** in DME giving a 58% yield of the alkylated sulfone **19** and a quantitative yield of the alkynyl carboethoxyketone **20** (eq. 6).



(5)

(16)

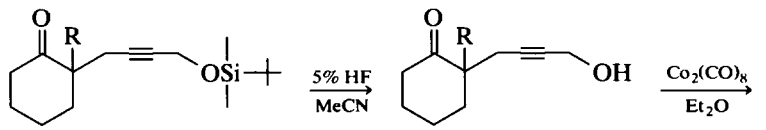


(6)

(**17**, R = SO_2Ph;
18, R = C(=O)–OEt)

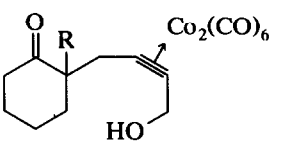
(**19**, R = SO_2Ph;
20, R = C(=O)–OEt)

Conversions of **16**, **19**, and **20** to the corresponding hydroxybutynyl ketones **21–23** were carried out in 5% HF/acetonitrile (eq. 7).



(**16**, R = C(=O)–Me;
19, R = SO_2Ph;
20, R = C(=O)–OEt)

(21–23)



(7)

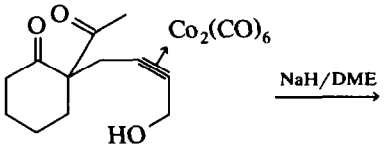
(**24**, R = C(=O)–Me;
25, R = SO_2Ph;
26, R = C(=O)–OEt)

The complexed hydroxybutynyl ketones **24–26** were again prepared by treating the corresponding hydroxybutynyl ketones **21–23** with $Co_2(CO)_8$ in ether. Attempts at cyclizing the hydroxybutynyl sulphone **25** were not successful. No reaction occurred at room temperature after 2 days. Upon refluxing decomposition of the cobalt complex was observed and only a small amount of the starting material was recovered.

We then attempted to lactonize complex **26**. In this case, one can envision two lactonization possibilities. The alkoxide generated from **26** may either attack the

ketone or the ester carbonyl leading in one case to the formation of the desired eleven-membered ring lactone, in the other to a seven-membered ring product. In fact, treatment of **26** with NaH at 45°C for 24 hours returned starting material; decomposition to uncharacterizable material occurred at higher temperatures.

In the case of the complexed diketone **24**, the above interesting possibility of addition to either of the two carbonyl groups is still present. Reaction at the cyclohexanone carbonyl would lead to the desired lactone **27**, while attack at the acetyl carbonyl would give rise to the acyclic ester **28** (eq. 8).



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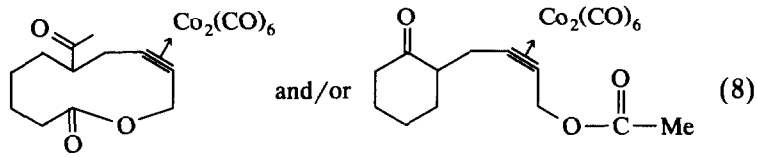
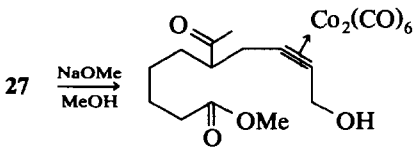


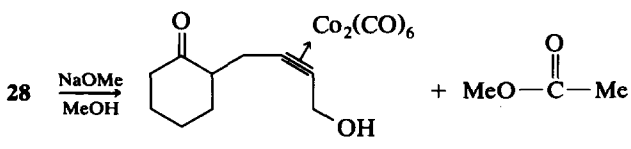
(8)

(27) **(28)**

This reaction was found to be very slow, even at 45°C; after 1 week it gave 21% yield of a single product, together with an equal amount of starting material. The product showed an absorption at 5.24 ppm (s, 2H, CH_2O); a doublet of doublets at 3.32 ppm ($J = 9$, 17 Hz, $COCHCH_2$); and a singlet at 1.77 ppm ($COCH_3$). The IR spectrum showed bands at 1746 cm^{-1} due to a *lactone* or *ester* group, and at 1714 cm^{-1} due to a ketone carbonyl. Reaction of this product with $NaOCH_3$ in CH_3OH gave only the result of transesterification, complexed hydroxybutynylcyclohexanone **30**; thus the product obtained in eq. 8 was the complexed ester **28** (eq. 9). Had the desired lactone been present, ring-opening to a hydroxyketoester would have been observed.



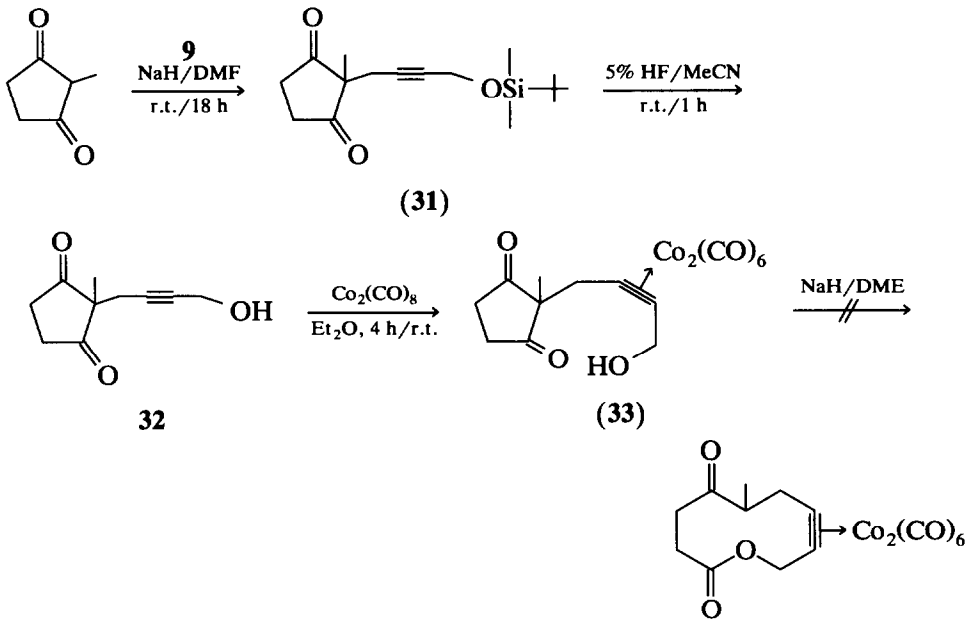
(29)



(9)

(30)

Assuming that the preferred conformation of **24** places the complexed butynyl side chain equatorial, attack of the alkoxide on either face of the cyclohexanone



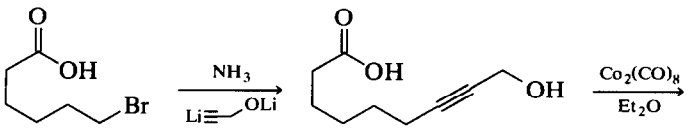
Scheme 3.

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 the reaction in systems **12** and **14**, where the second ring carbonyl in each of the two diones eliminates the interfering axial hydrogen.

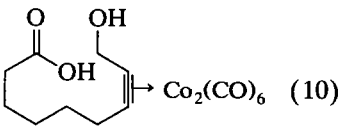
10-membered ring acetylenic lactone

To expand this work to 10-membered ring acetylenic lactones we alkylated 2-methyl-1,3-cyclopentanedione with **9** to give dione **31** in modest yield. Its structure was established spectroscopically. The silyloxybutynyl side chain showed the anticipated coupled triplets at 2.55 and 4.30 ppm. Deprotection of the hydroxyl group and complexation with octacarbonyldicobalt gave **33** in good yield. Attempts to cyclize **33** gave only uncharacterizable decomposition products, however, together with varying amounts of unreacted starting material Scheme 3).

Although several 2-hydroxy-2-phenylsulphonylcyclohexanones have been converted to lactones [5], approaches to 10-membered ring systems were not successful, presumably a result of ring strain. However, to find out if complexed 10-membered ring acetylenic lactones could be synthesized in other ways, we examined Mukaiyama's method [21]. We prepared 9-hydroxy-7-nonynoic acid [22c,23] **34** and treated it with dicobalt octacarbonyl, obtaining 87% yield of the complexed acid **35**. Decomplexation using ceric ammonium nitrate [24] in acetone returned the original acid, confirming that complexation had proceeded as expected (eq. 10).

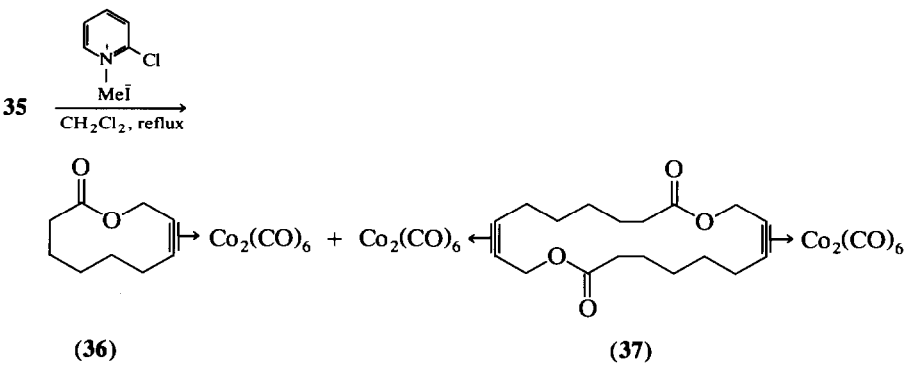


(34)



(35)

Qualitative small-scale attempts at cyclizing **35** in dilute solution using the Mukaiyama method succeed in forming the 10-membered ring acetylenic lactone **36**. On a preparative scale a 22% yield of **36** was obtained together with a 15% yield of the dimer **37** (eq. 11).



(36) (37)

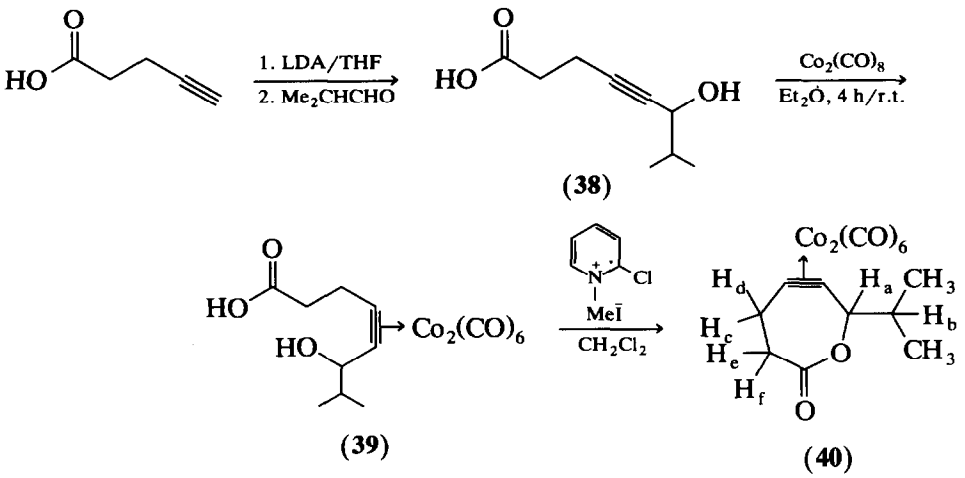
(11)

Molecular weight determination (isopiestic) and low resolution mass spectrometry were consistent with the monomeric formulation of **36**. The lactone carbonyl manifested a strong band in the IR at 1738 cm^{-1}.

7-membered ring acetylenic lactone

We turned next to preparing a complexed 7-membered ring lactone. Hydroxy acid [22c] **38** was complexed to give **39** in 81% yield. Again, decomplexation returned the original acid. Following Mukaiyama's procedure, **39** was readily lactonized to **40** (Scheme 4). Low resolution fast atom bombardment (FAB) mass spectrometry revealed an $M + H$ peak at 439 with 72% relative intensity. There was no trace of signals at higher molecular weight.

The structure of **40** was established by ^{1}H-NMR which revealed a doublet at 4.44 ppm ($J = 8.1$ Hz, 1H) for H_a due to coupling with H_b. The nonequivalent diastereotopic propargyl protons H_c and H_d revealed an interesting spectral feature. H_c exhibited a doublet of doublets at 2.55 ppm ($J_{cd} = 16.8$ Hz, $J_{ce} = 3.1$ Hz, $J_{cf} = 13.7$ Hz). A doublet of triplets at 2.39 ppm was assigned to proton H_d, split by H_c ($J = 16.8$ Hz) and by H_e and H_f ($J = 4$ Hz). H_e revealed a doublet of triplets at 2.16 ppm, derived from geminal coupling with H_f ($J = 12.4$ Hz) and equal coupling ($J = 4$ Hz) with H_c and H_d. H_f absorbed at 2.01 ppm as a triple set of doublets arising from vicinal coupling with H_c, geminal coupling with H_e



Scheme 4.

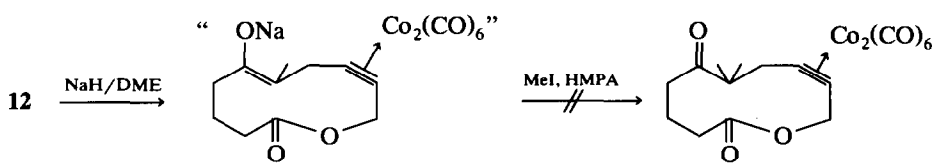
($J = 13$ Hz) and coupling with H_d ($J = 4.4$ Hz). The IR spectrum of the lactone exhibited the C=O stretch at 1741 cm^{-1}.

In the preparation of both the 10-membered ring lactone **36** and the 7-membered ring lactone **40**, considerable formation of cobalt salts was observed as well, probably due to oxidation by the chloropyridinium reagent. Therefore, it may be possible to improve the yields of the above lactonizations using alternative procedures that avoid this type of reagent, although we did not explore this possibility.

To summarize, the reaction of a variety of acetylenic hydroxycarbonyl compounds with dicobalt octacarbonyl gives rise to readily isolated cobalt-complexed alkynes. The change in geometry in the acetylenic unit upon complexation makes lactonization of these complexes by either base-induced intramolecular rearrangement (retro-Dieckmann reaction) or Mukaiyama's methodology possible.

Chemical behavior of lactone 13

With lactone **13** in hand, we proceeded to briefly explore its possible elaboration in several ways. Several attempts at alkylation of the substituted position α to the ketone by quenching the reaction mixture of the cobalt-complexed dione **12** by CH_3I with HMPA returned starting material (eq. 12).

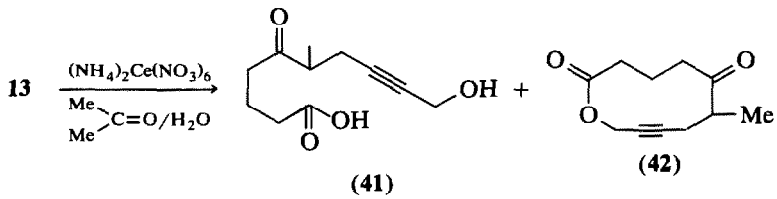


(12)

In order to determine whether the presumed enolate intermediate was too hindered for alkylation or was somehow protonated, **12** was added to NaH in DME and the mixture was stirred overnight before being quenched with D_2O. NMR analysis showed the formation of only *un*deuterated **13**. Thus the enolate does not persist long enough for alkylation to occur. Even carrying out the

lactonization itself in the presence of CH_3I fails. Attempts to trap the enolate with silyl chlorides were similarly unsuccessful. Evidently the lactone carbanion is protonated as soon as it forms, perhaps by OH hydrogens from unreacted **12**. We were also unsuccessful in adding nucleophiles selectively to the ketone carbonyl in **13**. Attempts using organomanganous [25,26], Wittig, and Grignard reagents all led to decomposition or recovery of unreacted starting material.

Addition of ceric ammonium nitrate to a solution of **13** in dry acetone resulted in vigorous gas evolution and a color change from dark red to pale yellow. After workup, NMR of the residue revealed the presence of more than one product. Chromatographic separation gave two fractions which were identified as the hydroxy acid **41** (5 to 10% yield) and the decomplexed 11-membered ring acetylenic lactone **42** isolated in 65–70% yield (eq. 13).



(13)

This process is reversible: re-complexation of **42** returns **13** quantitatively. In the ^{1}H-NMR, the propargyl methylenes of **42** are diastereotopic as expected, and the ^{13}C-NMR showed signals at 212 and 173 ppm; the acetylenic carbons absorbed at 86 and 79 ppm. The IR spectrum revealed bands at 2225 cm^{-1} (weak) for the acetylene, and 1744 and 1718 cm^{-1} for the carbonyls.

X-Ray structure of lactone 42

The result of single crystal X-ray diffraction analysis on **42** is shown in Fig. 1 [27]. It is, as expected, a monomeric ketolactone. Its ring possesses a slightly bent butynyl moiety with bond angles about the alkynyl carbons of 171.0° and 177.0°; the triple bond length is 1.190 Å. Through an *anti* alignment of the carbonyl groups

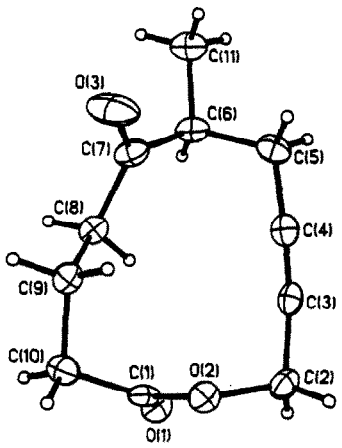


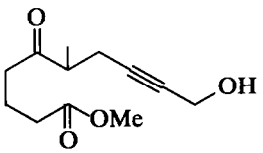
Fig. 1. Computer representation of $C_{11}H_{14}O_3$ (**42**).

the molecule avoids eclipsing interactions about the tetrahedral carbons and maintains near-normal bond lengths and bond angles. The methyl group is in a pseudo-equatorial position.

Chemical behavior of lactone 42

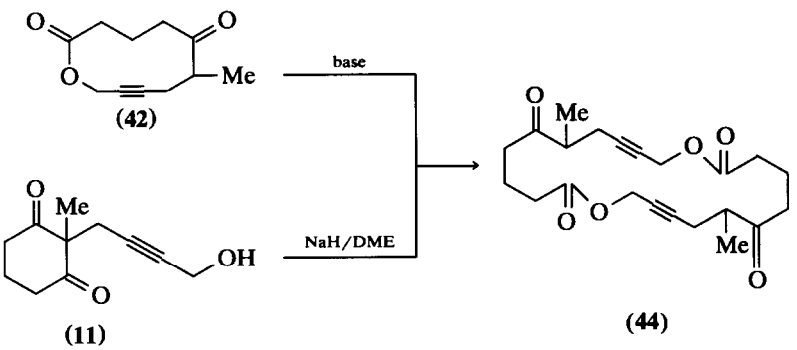
Attempted alkylation of **42** (NaH, CH_3I) led to a 72% yield of a white solid which appeared at first sight to be a methylated product. The IR showed bands at 1735 and 1718 cm^{-1} and ^{13}C-NMR signals at 212 and 172 ppm as well as 84 and 76 ppm for the acetylenic carbons. However, ^1H-NMR showed *two doublets* at 1.11 and 1.12 ppm of unequal intensity. Integration revealed that the ratio between the two doublets at 1.12 ppm and the methylene signal at 4.62 ppm was only 3:2, instead of the expected 3:1. Treatment of **42** with NaH in DME, then quenching with water gave the same product, confirming that alkylation had not occurred. Several additional alkylation attempts led to the conclusion that whenever **42** was treated with a base, the result was the same.

Separate treatment of this new compound and lactone **42** itself with $NaOCH_3$ in CH_3OH gave the same product. Its ^1H-NMR, ^{13}C-NMR and IR spectral data were consistent with the hydroxy ester **43**, suggestive of a dimeric or a polymeric formulation for the new compound.



(43)

Fortunately it was possible to crystallize this substance and obtain a single-crystal X-ray diffraction analysis, the result of which is discussed below [27*], the diolide **44**. Lactone **44** was also isolated as the only product in 68% yield when **11** was treated with NaH without prior cobalt complexation (eq. 14).



(42) **(11)** **(44)** (14)

X-ray structure of lactone 44

In the solid state **44** consists of a 1:1 mixture of two conformationally distinct macrocyclic dimers of **42**, one of which exists as a mixture of stereoisomers as well.

* Reference number with asterisk indicates a note in the list of references.

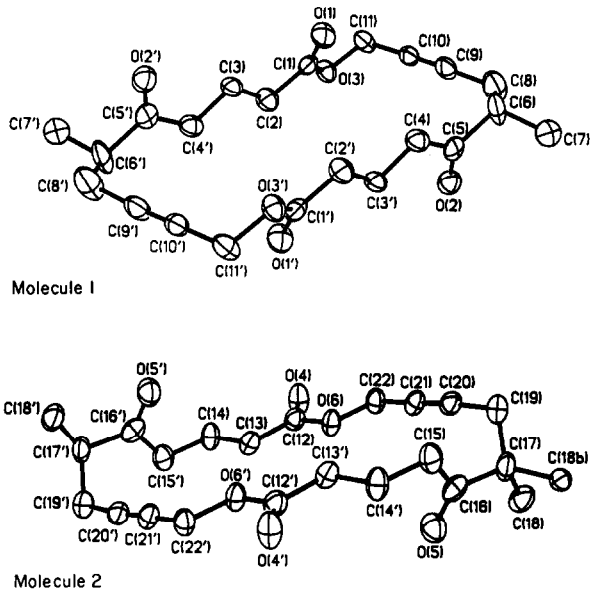
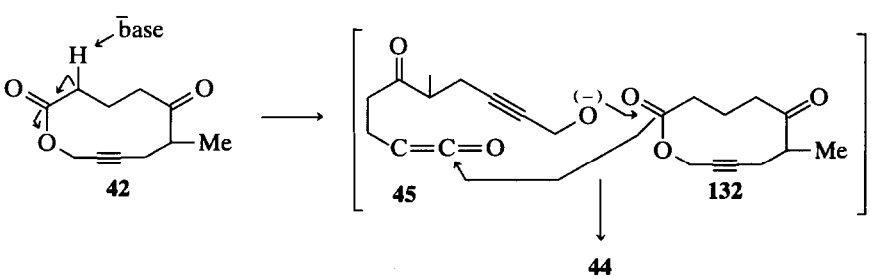


Fig. 2. Computer representation of two crystallographically distinct molecules of $C_{22}H_{28}O_6$ (**44**).

Molecule 1 is a centrosymmetric structure with *trans*, diequatorial methyl substituents (Fig. 2). Molecule 2 is disordered at the methyl substituent. Refinement of the occupancies of the alternative positions indicates that 79% are axial and 21% equatorial. The observation of two distinct methyl resonances in the NMR is consistent with the presence of both *cis* and *trans* isomers. Both molecules 1 and 2 exhibit nearly linear butynyl units (alkyne bond angles in the range 174.6–176.6°) with all bond lengths and angles in normal ranges. However, all four carbonyl groups in molecule 1 are pseudoaxial, while the keto carbonyls in molecule 2 are pseudoequatorial.

Any attempt to account for the formation of lactone **44** mechanistically is of necessity speculative. However, models based upon the X-ray structure of **42** show the molecule to be quite rigid. It is therefore difficult to see how intramolecular reversion to **11** could occur. Alternatively, proton abstraction from the methylene α to the lactone carbonyl in **42** could lead to the alkoxide ketene **45**. Attack at the lactone carbonyl of another molecule of **42** followed by intramolecular trapping of the newly generated alkoxide would lead to **44**.



As was the case with complexed lactone **13**, attempts to add nucleophilic reagents to the ketone in **42** met with no success. For example, Wittig reagents of several types [28,29] were unreactive, and attempts with Grignard, organolithium, and organomanganese reagents proved futile as well. Based on the crystal structure of **42**, the source of its low reactivity may be steric. The ketone possesses an axial orientation, and, if the molecule is as rigid in solution as molecular models seem to indicate, the top face is shielded by two axial hydrogens. The bottom face appears more accessible but may be blocked by the neighboring methyl group.

Conclusions

The general concept of exploiting geometry changes in organic functional groups upon metal complexation has seen occasional use in synthesis, and the specific application described here, alkyne bending by complexation to cobalt, has been used in carbocycle construction by both Schreiber [30] and Magnus [31]. Marshall [32] has also reported an application of cobalt complexation to protect a macrocyclic acetylenic ketoether from isomerization to a conjugated allene. In practice, we find that a variety of limitations combines to restrict the utility of the process in lactone synthesis. Nonetheless, when it succeeds the method is efficient and very simple to apply. The acetylene complexes are handled without special precautions and yields are generally synthetically viable. Thus, within the scope of substrates compatible with this methodology, it should be of use in the construction of medium-ring macrolide-based systems.

Experimental

General

Tetrahydrofuran (THF), benzene, diethyl ether, and dimethoxyethane (DME) were distilled from sodium benzophenone ketyl and stored over 4 Å sieves under dinitrogen. Dimethylsulfoxide (DMSO) and hexamethylphosphoramide (HMPA) were distilled under vacuum from CaH_2 before use. Dimethylformamide (DMF) was stored over 4 Å molecular sieves before use. Amines were distilled from calcium hydride and stored over 4 Å molecular sieves. Methyl iodide and allyl bromide were passed through a short column of neutral activated alumina, then distilled from calcium hydride. All other solvents and reagents were reagent grade and used as received without further purification. Melting points are uncorrected. Analytical samples were purified by chromatography on a Harrison Research Chromatotron or by recrystallization.

NMR spectra (^1H) were recorded on Varian EM-390 (90 MHz) or (^1H, 300 MHz and ^{13}C, 75 MHz, ^1H-decoupled) General Electric QE-300 spectrometers. Infrared spectra were recorded on an IBM FTIR/32 spectrophotometer. Elemental analyses were performed at the microanalytic laboratory at the University of California, Berkeley. High and low resolution mass spectral data were determined by Mr. Kei Miyano and Dr. A. Daniel Jones at the Facility for Advanced Instrumentation (FAI) at the University of California, Davis.

4-Bromo-1-(t-butyldimethylsilyloxy)-2-butyne (9) [33]. To a solution of 2-butyne-1,4-diol (34.44 g, 400 mmol) in DMF (150 mL) was added t-butyl-

dimethylsilylchloride (7.53 g, 50 mmol) and imidazole (6.81 g, 100 mmol). After stirring 17 h at 35–40°C, the mixture was quenched with water (200 mL) and extracted with ether (5 × 50 mL). The combined organic extracts were washed with saturated aqueous NH_4Cl (30 mL) and saturated aqueous NaCl (30 mL) and dried ($MgSO_4$). Evaporation afforded 9.30 g (93% based on t-butyldimethylsilylchloride) of 1-(t-butyldimethylsilyloxy)-2-butyn-4-ol, which was not purified further. ^{1}H-NMR ($CDCl_3$) δ 4.37 (t, $J = 1.5$ Hz, 2H), 4.30 (t, $J = 1.5$ Hz, 2H), 3.22 (br s, 1H), 0.93 (s, 9H), 0.14 (s, 6H); ^{13}C-NMR δ 83.23, 83.14, 51.44, 50.16, 25.48 (3C), 17.94, −5.55 (2C); IR (neat) 3405–3359, 1472, 1256, 1089 cm^{-1}. To a solution of this alcohol (8.00 g, 40 mmol) in ether (150 mL) were added CBr_4 (26.53 g, 80 mmol) and PPh_3 (20.98 g, 80 mmol). After stirring for 4 h, the reaction mixture was filtered through Celite and passed through Florisil using 20% ether in hexane. Evaporation gave 9.47 g (90%) of **9**, suitable for immediate use. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.34 (t, $J = 2$ Hz, 2H), 3.91 (t, $J = 2$ Hz, 2H), 0.88 (s, 9H), 0.10 (s, 6H); ^{13}C-NMR δ 83.32, 79.80, 51.73, 25.79 (3C), 18.24, 14.38, −5.18 (2C); IR (neat) 1472, 1256, 1089 cm^{-1}.

2-(4-[t-Butyldimethylsilyloxy]-2-butynyl)-2-methylcyclohexane-1,3-dione (10). To a suspension of NaH (1.0 g, 60% in oil, 25 mmol) in DMF (50 mL) at 0°C was added 2-methyl-1,3-cyclohexanedione (3.15 g, 25 mmol). The mixture was stirred for 15 min at 0°C, then **9** (7.90 g, 30 mmol) was added. The mixture was stirred at 25°C for 17 h, after which time it was quenched with saturated aqueous NH_4Cl (30 mL) and poured into a 1:1 water-CH_2Cl_2 mixture (100 mL). The organic phase was extracted with water (3 × 50 mL) and dried ($MgSO_4$). After removing the solvent, the residue was chromatographed on Florisil using 20% ether in hexane to yield 4.31 g (56%) of **10**. ^{1}H-NMR ($CDCl_3$) δ 4.19 (t, 2H, $J = 2.1$ Hz), 2.67 (t, 4H, $J = 6.8$ Hz), 2.63 (t, 2H, $J = 2.1$ Hz), 1.96 (quintet, 2H, $J = 6.8$ Hz), 1.27 (s, 3H), 0.86 (s, 9H), 0.06 (s, 6H); ^{13}C-NMR δ 209.03 (2C), 81.24, 80.71, 63.76, 51.62, 38.33 (2C), 25.57 (3C), 25.20, 21.64, 18.14, 17.17, −5.33 (2C); IR (neat) 1731, 1701, 1256, 1071 cm^{-1}. Anal. Found: C, 66.12; H, 9.14. $C_{17}H_{28}O_3Si$ calcd.: C, 66.19; H, 9.16%.

2-(4-Hydroxy-2-butynyl)-2-methylcyclohexane-1,3-dione (11). To a 5% HF in acetonitrile solution (9 mL, 9 mmol) was added **10** (2.77 g, 9 mmol). After stirring at 25°C for 1 h, $CHCl_3$ (50 mL) was added and the reaction mixture was extracted with water (4 × 30 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo* to afford 1.51 g (7.8 mmol, 87%) of **11**, which was used without further purification. ^{1}H-NMR ($CDCl_3$) δ 4.20 (t, $J = 2.1$ Hz, 2H), 2.67 (m, 6H), 1.97 (m, 2H), 1.80 (br s, 1H), 1.28 (s, 3H); ^{13}C-NMR δ 209.28 (2C), 81.17, 80.88, 63.78, 50.44, 37.97 (2C), 24.89, 21.60, 16.96; IR (neat) 3463, 1728, 1698 cm^{-1}.

2-(4-Hydroxy-2-butynyl)-2-methylcyclohexane-1,3-dione hexacarbonyldicobalt complex (12). To a solution of dicobaltoctacarbonyl (5.64 g, 16.5 mmol) in anhydrous ether (100 mL) was added **11** (3.10 g, 15 mmol). After stirring for 4 h at 25°C, the mixture was concentrated and the residue chromatographed on Florisil using hexane to remove the unreacted dicobaltoctacarbonyl, followed by ether. Concentration gave 4.10 g (57%) of dark red crystalline **12**. ^{1}H-NMR (C_6D_6) δ 4.39 (d, $J = 5.6$ Hz, 2H), 3.38 (s, 2H), 2.12 (m, 4H), 1.15 (m, 2H), 1.12 (t, $J = 5.6$ Hz, 1H), 0.80 (s, 3H); ^{13}C-NMR δ 208.28 (2C), 200.18 (6C), 97.88, 91.68, 66.65, 63.60, 39.13, 37.30 (2C), 25.05, 17.17; IR (C_6D_6) 3449, 2052, 2025, 1730, 1700 cm^{-1}; m.p. 92–94°C. Anal. Found: C, 42.52; H, 2.96. $C_{17}H_{14}Co_2O_9$ calcd.: C, 42.51; H, 2.94%.

7-Methyloxacyclo-9-undecyne-2,6-dione hexacarbonyldicobalt complex (13). To a suspension of NaH (0.17 g, 4.2 mmol) in DME (20 mL) was added **12** (1.92 g, 4 mmol). After stirring overnight, the mixture was poured into 2% acetic acid in water (50 mL) and extracted with ether (3 × 25 mL). The combined organic extracts were washed with water (2 × 30 mL) and dried (Na_2SO_4). Concentration gave 1.37 g (2.85 mmol, 71% yield) of **13** as a dark red viscous oil. ^{1}H-NMR (C_6D_6) δ 5.38 (d, J = 13 Hz, 1H), 4.58 (d, J = 13 Hz, 1H), 3.36 (dd, J = 15.1, 11.6 Hz, 1H), 2.41 (br d, J = 15.1 Hz, 1H), 2.34–0.80 (m, 7H), 0.63 (d, J = 7.1 Hz, 3H); ^{13}C-NMR δ 210.11, 200.10 (6C), 171.06, 97.10, 89.89, 64.71, 47.81, 40.68, 38.21, 35.50, 19.14, 19.05; IR (neat) 2094, 2059, 1745, 1718 cm^{-1}.

2-Allyl-2-(4-hydroxy-2-butynyl)cyclohexane-1,3-dione hexacarbonyldicobalt complex (14). To a solution of potassium metal (1.0 g, 25 mmol) in absolute ethanol (20 mL) was added 2-allyl-1,3-cyclohexanedione (3.80 g, 25 mmol). The reaction mixture was warmed and to the clear solution thus obtained was added **9** (7.23 g, 27.5 mmol). The mixture was refluxed for 8 h until no longer alkaline. After cooling, the KBr was removed by filtration. The filtrate was concentrated taken up in ether (80 mL). This solution was washed with dilute Na_2CO_3 (20 mL), and water (20 mL), and dried ($MgSO_4$). After concentration, the residue was chromatographed on silica using 10% ether in hexane to yield 5.0 g (15 mmol, 60%) of the product, 2-allyl-2-(4-[t-butyldimethylsilyloxy]-2-butynyl)cyclohexane-1,3-dione. ^{1}H-NMR ($CDCl_3$) δ 5.56 (m, 1H), 5.3–4.9 (m, 2H), 4.25 (t, J = 2 Hz, 2H), 2.9–2.2 (m, 8H), 2.05 (m, 2H), 0.95 (s, 9H), 0.15 (s, 6H); IR (neat) 3081, 1728, 1700, 1640, 1256, 1080 cm^{-1}. Anal. Found: C, 67.90; H, 8.95. $C_{19}H_{30}O_3Si$ calcd.: C, 68.22; H, 9.05%. Following the procedure used for **11**, this dione (3.34 g, 10 mmol), was desilylated to give 2-allyl-2-(4-hydroxy-2-butynyl)cyclohexane-1,3-dione in 98% yield. ^{1}H-NMR ($CDCl_3$) δ 5.50 (m, 1H), 5.1–4.7 (m, 2H), 4.10 (m, 2H), 2.7–2.1 (m, 8H), 1.90 (m, 2H), 1.10 (t, J = 3 Hz, 1H, OH); IR (neat) 3438, 3080, 1697, 1640 cm^{-1}. Following the procedure used for **12**, this dione-alcohol (1.79 g, 5.2 mmol), was complexed to give **14** in a 53% yield. ^{1}H-NMR (C_6D_6) δ 5.40–4.70 (m, 3H), 4.40 (d, J = 4 Hz, 2H), 3.50 (s, 3H), 2.20–1.90 (m, 5H), 1.40–0.80 (m, 2H); IR (C_6D_6) 3592, 3080, 2016, 1731, 1699, 1640 cm^{-1}.

7-Allyloxacyclo-9-undecyne-2,6-dione hexacarbonyldicobalt complex (15). In a manner similar to that described for **13**, **14** (1.15 g, 2.3 mmol) was lactonized to give **15** in 50% yield. ^{1}H-NMR (C_6D_6) δ 5.53 (m, 1H), 5.49 (d, J = 13 Hz, 1H), 4.99 (d, J = 10 Hz, 1H), 4.94 (dd, J = 1, 17 Hz, 1H), 4.71 (d, J = 13 Hz, 1H), 3.53 (dd, J = 11.4, 15 Hz, 1H), 2.79 (d, J = 15 Hz, 1H), 2.63 (m, 1H), 2.40–1.70 (m, 6H), 1.35 (m, 2H); IR (C_6D_6) 3081, 2092, 2013, 1747, 1719, 1641 cm^{-1}. Anal. Found: C, 45.07; H, 3.35. $C_{19}H_{16}Co_2O_9$ calcd.: C, 45.07; H, 3.19%.

2-Acetyl-2-(4-[t-butyldimethylsilyloxy]-2-butynyl)cyclohexanone (16). Following the procedure used for **10**, 2-acetylcyclohexanone (1.40 g, 10 mmol) was alkylated with **9** (3.16 g, 12 mmol) to yield 1.76 g (6 mmol, 95%) of **16**. ^{1}H-NMR ($CDCl_3$) δ 4.30 (t, J = 1.5 Hz, 2H), 2.75 (m, 2H), 2.35 (m, 2H), 2.20 (s, 3H), 1.75 (m, 6H), 0.95 (s, 9H), 0.15 (s, 6H); IR (neat) 1720, 1701, 1253, 1080 cm^{-1}.

2-Carboethoxy-2-(4-[t-butyldimethylsilyloxy]-2-butynyl)cyclohexanone (20). In a manner similar to that used above, 2-carboethoxycyclohexanone (1.70g , 10 mmol) was alkylated with **9** (3.16 g, 12 mmol) in DME to give 3.5 g (10 mmol, 100%) of **20**. ^{1}H-NMR ($CDCl_3$) δ 4.4–4.1 (m, 4H), 2.9–2.3 (m, 4H), 1.9–1.4 (m, 6H), 1.35 (t, J = 5 Hz, 3H), 0.95 (s, 9H), 0.15 (s, 6H); IR (neat) 1716, 1256, 1071 cm^{-1}.

2-Phenylsulfonyl-2-(4-[t-butyldimethylsilyloxy]2-butynyl)cyclohexanone (19). Following the general procedure, 2-phenylsulfonylcyclohexanone (1.19 g, 5 mmol) was alkylated with **9** (1.58 g, 6 mmol) in DME to yield 1.22 g (2.9 mmol, 58%) of **19**. ^{1}H-NMR ($CDCl_3$) δ 8.0–7.5 (m, 5H), 4.25 (t, $J = 1$ Hz, 2H), 3.4–1.6 (m, 10H), 0.95 (s, 9H), 0.15 (s, 6H); IR (neat) 3067, 1709, 1309, 1256, 1156 cm^{-1}. Anal. Found: C, 62.80; H, 7.49. $C_{22}H_{32}O_4SiS$ calcd.: C, 62.83; H, 7.68%.

2-Acetyl-2-(4-hydroxy-2-butynyl)cyclohexanone (21). In a manner similar to that described for **11**, **16** (3.22 g, 10 mmol) was desilylated to give **21** in 95% yield. ^{1}H-NMR ($CDCl_3$) δ 4.15 (t, $J = 1.5$ Hz, 2H), 2.60 (m, 2H), 2.20 (m, 2H), 2.05 (s, 3H), 1.60 (m, 6H); IR (neat) 3450, 1694 cm^{-1}.

2-Carboethoxy-2-(4-hydroxy-2-butynyl)cyclohexanone (23). In a manner similar to that above, **20** (3.50 g, 10 mmol) was desilylated to give **23** in 99% yield. ^{1}H-NMR ($CDCl_3$) δ 4.25–4.00 (m, 4H), 2.65–2.25 (m, 4H), 2.1–1.3 (m, 6H), 1.25 (t, $J = 5$ Hz, 3H); IR (neat) 3530, 1714 cm^{-1}.

2-Phenylsulfonyl-2-(4-hydroxy-2-butynyl)cyclohexanone (22). Following the general procedure, **19** (2.10 g, 5 mmol) was desilylated to give **22** in 98% yield. ^{1}H-NMR ($CDCl_3$) δ 7.8–7.3 (m, 5H), 4.10 (t, $J = 1$ Hz, 2H), 3.2–1.5 (m, 10H); IR (neat) 3518, 3067, 1709, 1308, 1140 cm^{-1}.

2-Acetyl-2-(4-hydroxy-2-butynyl)cyclohexanone hexacarbonyldicobalt complex (24). In a manner similar to that described for **12**, **21** (1.04 g, 5 mmol) was complexed to give **24** in 75% yield. ^{1}H-NMR (C_6D_6) δ 4.50 (d, $J = 5$ Hz, 2H), 3.35 (d, $J = 15$ Hz, 1H), 3.15 (d, $J = 15$ Hz, 1H), 2.40 (t, $J = 5$ Hz, 1H), 2.00 (m, 2H), 1.75 (s, 3H), 1.30–0.60 (m, 6H); IR (C_6D_6) 3477, 2091, 2052, 1700, 1653 cm^{-1}.

2-Carboethoxy-2-(4-hydroxy-2-butynyl)cyclohexanone hexacarbonyldicobalt complex (26). In a manner similar to that above, **23** (1.57 g, 6 mmol) was complexed to give **26** in 52% yield. ^{1}H-NMR (C_6D_6) δ 4.55 (d, $J = 5$ Hz, 2H), 3.90 (q, $J = 5$ Hz, 2H), 3.30 (m, 2H), 1.6–1.1 (m, 4H), 0.85 (t, $J = 5$ Hz, 3H); IR (C_6D_6) 3539, 2090, 2051, 2022, 1717 cm^{-1}.

2-Phenylsulfonyl-2-(4-hydroxy-2-butynyl)cyclohexanone hexacarbonyldicobalt complex (25). Following the general procedure, **22** (1.37 g, 4.5 mmol) was complexed to give **25** in 72% yield. ^{1}H-NMR (C_6D_6) δ 7.8–7.5 (m, 2H), 7.1–6.8 (m, 3H), 4.35 (d, $J = 5$ Hz, 2H), 3.75 (d, $J = 14$ Hz, 1H), 3.30 (d, $J = 14$ Hz, 1H), 3.0–0.80 (m, 8H); IR (C_6D_6) 3580, 2024, 1705, 1309, 1137 cm^{-1}.

Attempted lactone formation from 24. To a suspension of NaH (0.056 g, 1.4 mmol) in DME (20 mL) was added **24** (0.70 g, 1.4 mmol). After stirring for 1 week at 40°C, the reaction mixture was poured onto 2% acetic acid in water (50 mL) and extracted with ether (3 × 25 mL). The combined organic extracts were washed with water (2 × 30 mL) and dried (Na_2SO_4). Concentration gave 0.15 g (20% yield) of a dark red viscous oil consisting of the product **28** together with *ca.* 20% starting material. ^{1}H-NMR (300 MHz, C_6D_6) δ 5.24 (s, 2H), 3.32 (dd, $J = 9$, 17 Hz, 1H), 2.5–2.0 (m, 4H), 1.77 (s, 3H), 1.5–0.7 (m, 6H); IR (C_6D_6) 2092, 2013, 1746, 1714 cm^{-1}; low-resolution MS, *m/z* (rel intensity) 438 (19.6, $M - 2CO$), 410 (56.7, $M - 3CO$), 383 (24.1), 382 (64.1, $M - 4CO$), 354 (28.2, $M - 5CO$), 327 (51.8), 326 (75.8, $M - 6CO$), 270 (34.9), 236 [58.4, $M - Co_2(CO)_5$], 216 (51.2), 208 [66.2, $M - Co_2(CO)_6 = C_{12}H_{16}O_3$], 178 (48.9), 149 [75.0, $M - Co_2(CO)_6$–OAc = $C_{10}H_{13}O$], 97 (55.6, C_6H_9O), 83 (55.6), 69 (57.2), 55 (69.0); high-resolution MS Found 437.9596. $C_{16}H_{16}Co_2O_7$ ($M - 2CO$) calcd. 437.9560.

Preparation and attempted lactonization of 2-(4-hydroxy-2-butynyl)-2-methyl-

cyclopentane-1,3-dione hexacarbonyldicobalt complex (33). Following the general procedure, 2-methyl-1,3-cyclopentanedione (2.24 g, 20 mmol) was alkylated with **9** (5.79 g, 22 mmol) to yield 1.76 g (6 mmol, 30%) of **31**. ^{1}H-NMR ($CDCl_3$) δ 4.30 (t, J = 1.5 Hz, 2H), 2.90 (s, 4H), 2.55 (t, J = 1.5 Hz, 2H), 1.20 (s, 3H), 0.95 (s, 9H), 0.15 (s, 6H); IR (neat) 1769, 1730, 1256, 1071 cm^{-1}. Without further purification **31** (1.47 g, 5 mmol) was desilylated in the usual way to afford **32** in a 90% yield. ^{1}H-NMR ($CDCl_3$) δ 4.05 (t, J = 1.5 Hz, 2H), 2.75 (s, 4H), 2.40 (t, J = 1.5 Hz, 2H), 1.05 (s, 3H); IR (neat) 3485, 1769, 1730 cm^{-1}. As described above, **31** (0.54 g, 3 mmol) was complexed, giving **33** in a 50% yield. ^{1}H-NMR (C_6D_6) δ 4.50 (d, J = 5 Hz, 2H), 3.20 (s, 2H), 2.90 (t, J = 5 Hz, 1H), 2.25 (s, 4H), 0.80 (s, 3H); IR (C_6D_6) 3547, 2093, 2053, 1768, 1730 cm^{-1}. Several attempts to elicit lactonization from **33** under the conditions described for **13** and **15** afforded no characterizable products.

Oxacyclo-8-decyn-2-one hexacarbonyldicobalt complex (36). The precursor, 9-hydroxy-7-nonynoic acid [22c], was prepared as follows. To 120 mL of NH_3 at −78°C was added lithium (1.05 g, 150 mmol). To the resulting blue solution was added dropwise 2-propynol (4.20 g, 4.4 mL, 75 mmol) and the mixture was refluxed at −33°C for 1 h. After this time, 6-bromohexanoic acid (3.51 g, 18 mmol) in THF (50 mL) was added and the mixture was refluxed for an additional 8 h and left to evaporate. The residue was quenched with 5N HCl (50 mL), extracted with ether (4 × 30 mL) and dried ($MgSO_4$). Evaporation of the solvent gave 2.60 g (15.3 mmol, 85% yield) of the acid as a white solid. ^{1}H-NMR $CDCl_3$) δ 6.6 (br s, 2H), 4.25 (t, J = 1.5 Hz, 2H), 2.6–2.1 (m, 4H), 1.8–1.4 (m, 6H); IR ($CDCl_3$) 3613, 3584, 2677, 1710 cm^{-1}; m.p. 44–45°C. This acid (0.51 g, 3.0 mmol) was added to a solution of dicobaltoctacarbonyl (1.13 g, 3.3 mmol) in anhydrous ether (30 mL). After stirring for 4 h at 25°C, the solvent was evaporated and the residue chromatographed on Florisil. Hexane eluted unreacted dicobaltoctacarbonyl. Elution with ether gave 0.63 g of the complexed acid **35**. The column was then flushed with methanol eluent to give another 0.54 g of **35**. The combined material was dried under vacuum to afford 1.17 g (2.6 mmol, 87% yield). ^{1}H-NMR data of this compound were not obtained because of its apparent ease of decomposition into paramagnetic species. However, demetallation gave a product which was identical to an authentic sample of 9-hydroxy-7-nonynoic acid. IR (neat) 3629–2665, 2937, 2090, 2014, 1712 cm^{-1}. To a solution of **35** (0.456 g, 1 mmol) in dry CH_2Cl_2 (100 mL) was added triethylamine (0.80 g, 1.10 mL, 8 mmol), and the resulting solution was added slowly (over 8 h) *via* a syringe pump to a refluxing solution of 2-chloro-1-methylpyridinium iodide (1.02 g, 4 mmol) in CH_2Cl_2 (100 mL). After the addition was complete, the mixture was refluxed for an additional 30 min. Evaporation of the solvent gave a residue which was chromatographed on silica. The hexane eluent was concentrated to give 0.094 g (22% yield) of oxacyclo-8-decyn-2-one hexacarbonyldicobalt complex (**36**). Concentration of the 1:9 ether–hexane eluent gave 0.063 g (15% yield) of the diolide **37**. For **36**, ^{1}H-NMR (C_6D_6) δ 5.11 (s, 2H), 2.51 (t, J = 5.6 Hz, 2H), 1.92 (t, J = 4.8 Hz, 2H), 1.46 (br m, 2H), 1.36 (m, 2H), 1.18 (m, 2H); IR (neat) 2092, 2021, 1738 cm^{-1}; low-resolution MS, m/z (rel intensity) 438 (5.5, M), 410 (3.0, M − CO), 382 (76.5, M − 2CO), 354 (81.8, M − 3CO), 326 (89.5, M − 4CO), 298 (82.6, M − 5CO), 270 (100.0, M − 6CO), 242 (27.1, M − 7CO), 228 (23.4, M − 7CO − CH_2), 226 (19.2, M − 6CO − CO_2), 224 (45.9), 216 (28.5), 200 (11.0, M − 7CO − 3CH_2), 198 (17.8, M − 6CO − CO_2 − 2CH_2), 196 (16.8), 188 (19.4), 184 (20.5, M − 6CO − CO_2 − 3CH_2), 172 (18.4,

$M - 7CO - 5CH_2$), 170 (13.8, $M - 6CO - CO_2 - 4CH_2$), 156 (22.3, $M - 6CO - CO_2 - 5CH_2$), 143 (26.0, Co_2C_2H), 137 (31.4), 118 (78.5, Co_2).

A molecular weight determination using the isopiestic [34] method was carried out as follows: a solution of 15.3 mg 4-bromobiphenyl (mol. wt. 233, Eastman) in *ca.* 1.4 mL ether (approx. 0.054 *M*) was prepared and loaded into one arm of the Signer apparatus, which had been fitted with Teflon valves. A solution containing 41.4 mg of **36**, also in *ca.* 1.4 mL ether (approx. 0.071 *M* if a monomer, 0.036 M if a dimer) was loaded in the other arm. After 7 days the volume of the standard solution had dropped to 1.24 mL, that of the sample had risen to 1.61 mL. After two more weeks equilibration (*i.e.*, to equal solute concentrations) appeared to have been reached asymptotically at *V*(standard) = 1.19 mL, *V*(sample) = 1.66 mL, resulting in a value for the molecular weight of **36** of 448 ± 25.

7-Isopropyloxacyclo-5-heptyn-2-one hexacarbonyldicobalt complex (40). The precursor, 6-hydroxy-7-methyl-4-octynoic acid [22c], was prepared as follows. To a solution of freshly distilled dry diisopropylamine (2.35 mL, 1.68 mmol) in dry THF (20 mL) at 0°C, was added dropwise n-butyllithium (1.6 *M* in hexane, 11 mL) *via* syringe such that the temperature of the reaction was maintained below 5°C. The resulting solution was stirred for 10 min at 0°C and then cooled to −40°C, whereupon a solution of 4-pentynoic acid (0.77 g, 7.9 mmol) in dry THF (10 mL) was added dropwise over 10 min followed by addition in one portion of HMPA (7 mL). The resulting white suspension was stirred for 10 min at −30°C, and to this was added in one portion freshly distilled isobutyraldehyde (0.73 mL, 8 mmol). The resulting clear yellow solution was allowed to warm to 0°C, where it was poured into a mixture of ether and water. The ether layer was extracted with saturated $NaHCO_3$ (2 × 20 mL). The combined aqueous layers were neutralized with conc. HCl and then extracted with ether (3 × 40 mL) and dried ($MgSO_4$). Concentration gave 1.16 g (6.85 mmol, 87% yield) of the acid **38**. ^{1}H-NMR ($CDCl_3$) δ 4.46 (br s, 2H), 4.12 (br d, J = 5.4 Hz, 1H), 2.53 (br s, 4H), 1.80 (m, 1H), 0.99 (d, J = 4.5 Hz, 3H), 0.97 (d, J = 4.5 Hz, 3H); IR ($CDCl_3$) 3694, 3612–2600, 2965, 1716 cm^{-1}. In a manner similar to that above, the acid (0.55 g, 3.2 mmol) was complexed to give **39** in an 81% yield. IR (C_6D_6) 3594, 3590–2521, 2022, 1714 cm^{-1}. Following the procedure for **36**, **39** (92 mg, 0.20 mmol) was lactonized, giving **40** in 28% yield. ^{1}H-NMR (C_6D_6) δ 4.44 (d, J = 8.1 Hz, 1H), 2.55 (ddd, J = 3.1, 13.7, 16.8 Hz, 1H), 2.39 (dt, J_d = 16.8 Hz, J_t = 4 Hz, 1H), 2.16 (dt, J_d = 12.4 Hz, J_t = 3 Hz, 1H), 2.01 (dt, J_d = 4.4 Hz, J_t = 13 Hz, 1H), 1.91 (m, 1H), 1.03 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H); IR (C_6D_6) 2098, 2059, 2032, 1741 cm^{-1}; low-resolution MS, *m/z* (rel intensity) 438 (0.7, *M*), 410 (11.8, $M - CO$), 382 (26.9, $M - 2CO$), 354 (11.2, $M - 3CO$), 327 (11.7), 326 (94.7, $M - 4CO$), 298 (42.7, $M - 5CO$), 270 (100.0, $M - 6CO$), 228 (37.7, $M - 7CO - CH_2$ or $M - 6CO - C_3H_6$), 226 (13.4, $M - 6CO - CO_2$), 196 (10.4), 151 (17.9, $M - Co_2(CO)_6 - H$), 149 (28.6), 137 (19.2), 118 (27.6, Co_2); low-resolution fast atom bombardment (FAB) MS, *m/z* (rel intensity) 439 (72, $M + H$), 410 (48, $M - CO$), 383 (86, $M + H - 2CO$), 382 (68, $M - 2CO$), 355 (94, $M + H - 3CO$), 326 (100, $M - 4CO$), no trace of signals assignable to higher molecular weight oligomers; high-resolution MS Found 409.9238. $C_{14}H_{12}Co_2O_7$ ($M - CO$) calcd. 409.9247.

7-Methyloxacyclo-9-undecyne-2,6-dione (42). To a solution of lactone **13** (1.5 g, 3.13 mmol) in dry acetone (100 mL) at 25°C was added $(NH_4)_2Ce(NO_3)_6$ (8.60 g, 15.65 mmol). The mixture was stirred until CO evolution ceased (*ca.* 5 min). Water

(100 mL) was added and the mixture was extracted with ether (3 × 50 mL). The combined organics were washed with brine (2 × 30 mL) and then dried over Na_2SO_4. After concentration the products were separated on Florisil. Concentration of the ether fraction gave **42** as a white solid (425 mg, 70%). A methanol eluent gave hydroxy acid **41** as a pale yellow oil (34 mg, 5%). For **41**, ^{1}H-NMR ($CDCl_3$) δ 4.25 (s, 2H), 2.70 (m, 3H), 2.43 (m, 4H), 1.93 (m, 2H), 1.16 (d, J = 7 Hz, 3H); IR (neat) 3406–2500, 1720, 1320, 1257, 1233 cm^{-1}. For **42**, ^{1}H-NMR ($CDCl_3$) δ 4.65 (dt, J_d = 15 Hz, J_t = 2.5 Hz, 1H), 4.55 (ddd, J = 1.5, 2.5, 15 Hz, 1H), 2.87 (ddq, J_d = 6.3, 9.6 Hz, J_q = 6.9 Hz, 1H), 2.80–2.20 (m, 7H), 1.90 (m, 1H), 1.05 (d, J = 6.9 Hz, 3H); ^{13}C-NMR δ 212.6, 173.4, 85.8, 79.1, 52.6, 45.1, 40.8, 34.3, 23.8, 18.7, 16.3; IR ($CDCl_3$) 1744, 1718, 1256, 1232 cm^{-1}; low-resolution fast atom bombardment (FAB) MS, m/z 195 (M + H); m.p. = 55–56°C. Anal. Found: C, 68.24; H, 7.44. $C_{11}H_{14}O_3$ calcd.: C, 68.01; H, 7.27%.

7,18-Dimethyl-1,12-dioxacyclodocosa-9,20-diyne-2,6,13,17-tetraone (44). To a suspension of NaH (40 mg, 1 mmol, 60% in oil) in DME (3 mL) was added lactone **42** (194 mg, 1 mmol) in DME (2 mL). After stirring for 20 min, water was added (10 mL) and the result was extracted with ether (2 × 10 mL) and dried over Na_2SO_4. Concentration under reduced pressure gave lactone **44** as a white solid (140 mg, 72%). ^{1}H-NMR ($CDCl_3$) δ 4.62 (m, 4H), 2.73 (m, 2H), 2.60 (m, 4H), 2.46–2.28 (m, 8H), 2.02–1.80 (m, 4H), 1.13 (d, J = 6.9 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H); ^{13}C-NMR δ 211.7, 172.4, 84.5, 76.1, 52.4, 45.2, 45.1, 40.7, 40.4, 32.9, 22.8, 22.7, 18.5, 16.3; IR ($CDCl_3$) 2928, 1735, 1717, 1700, 1696, 1261, 1155, 1018 cm^{-1}; m.p. = 118–120°C. Anal. Found: C, 68.03; H, 7.44. $C_{22}H_{28}O_6$ calcd.: C, 68.01; H, 7.27%.

7,18-Dimethyl-1,12-dioxacyclodocosa-9,20-diyne-2,6,13,17-tetraone (44) from 11. To a suspension of NaH (40 mg, 1 mmol, 60% in oil) in DME (3 mL) was added hydroxy dione **11** (194 mg, 1 mmol) in DME (2 mL). After the evolution of H_2 ceased, the mixture was stirred for 16 h. Water was then added (10 mL), the mixture was extracted with ether (2 × 10 mL), and dried over Na_2SO_4. Concentration under reduced pressure gave lactone **44** as a white solid (132 mg, 0.34 mmol, 68%), identical in all respects to that obtained from **42**.

X-ray crystal structure determination for 7-methyloxacyclo-9-undecyne-2,6-dione (42). Crystals were air-stable colorless plates, many twinned or with small cracks. One with dimensions 0.37 × 0.20 × 0.10 mm was mounted and data collected at 130 K in a stream of N_2. The triclinic space group $P\bar{1}$ was established and data collected on a Syntex $P2_1$ diffractometer (see Table 1 for complete crystal data and data collection parameters). Data for 1811 reflections were obtained using an ω scan with a scan speed of 15 deg min^{-1}, with a 2 deg scan width and 1.5 deg offset backgrounds in the range $2\theta < 50°$. The structure was solved by direct methods [35*,36*]. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions using a riding model, with C–H of 0.96 Å and $U_H = 1.2\ U^*_C$. The largest feature on a final difference map was 0.22 e Å^{-3} in height, and the largest shift in the final cycle of refinement was 0.059 for U_{12} of C(10). Final $R = \Sigma \| F_o | - | F_c \| / | F_o | = 0.048$ and $R_w = \Sigma \| F_o | - | F_c \| w^{1/2} / \Sigma | F_o w^{1/2} | = 0.044$, with $w = (\sigma^2(F_o) + 0.00031 F_o^2)^{-1}$.

Atomic coordinates are given in Table 2 and bond distances and angles in Table 3.

Table 1

Crystal data and data collection parameters for $C_{11}H_{14}O_3$ (**42**)

Formula	$C_{11}H_{14}O_3$
FW	194.23
Color and habit	colorless plates
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	5.808 (1)
b, Å	5.588 (1)
c, Å	15.953 (2)
α, deg	87.94 (1)
β, deg	94.15 (1)
γ, deg	99.97 (1)
V, Å^3	508.5 (1)
T, K	130
Z	2
Crystal dimensions, mm	$0.37 \times 0.20 \times 0.10$
$d_{calcd.}$, g cm^{-3}	1.27
Radiation, (Å)	Mo-K_α, ($\lambda = 0.71069$)
μ (Mo-K_α), cm^{-1}	0.86
Range of transmission factors	0.98–0.99
Diffractometer	$P2_1$, graphite monochromator
Scan method	ω, 2.0° range, 1.5° offset for background
Scan speed, deg min^{-1}	15.0
2θ range, deg	0–50
Octants collected	$h, \pm k, \pm l$
No. data collected	1811
No. unique data	1787 [R(merge) = 0.009]
No. data used in refinement	1217 [$I > 2\sigma(I)$]
No. parameters refined	130
R	0.048
R_w	0.044 [$w = (\sigma^2(F_o) + 0.00031F_o^2)^{-1}$]

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å$^2 \times 10^3$) for $C_{11}H_{14}O_3$ (**42**)

	x	y	z	U [a]
O(1)	2530(3)	2589(3)	4457(1)	27(1)
O(2)	987(3)	5896(3)	4054(1)	25(1)
O(3)	−1302(4)	2892(5)	1208(1)	50(1)
C(1)	862(5)	3484(5)	4201(2)	22(1)
C(2)	3322(5)	7209(5)	3913(2)	27(1)
C(3)	3819(4)	6729(5)	3053(2)	25(1)
C(4)	3919(5)	6157(5)	2347(2)	27(1)
C(5)	3932(5)	5351(5)	1480(2)	32(1)
C(6)	2752(5)	2688(5)	1341(2)	26(1)
C(7)	312(5)	2326(5)	1646(2)	28(1)
C(8)	−23(5)	1290(5)	2524(2)	25(1)
C(9)	−1887(5)	2278(5)	2972(2)	27(1)
C(10)	−1514(5)	2125(5)	3937(2)	27(1)
C(11)	2762(5)	2105(5)	417(2)	35(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3

Bond lengths (Å) and angles (°) for $C_{11}H_{14}O_3$ (**42**)

O(1)–C(1)	1.205(3)	O(2)–C(1)	1.350(3)
O(2)–C(2)	1.455(3)	O(3)–C(7)	1.208(3)
C(1)–C(10)	1.495(4)	C(2)–C(3)	1.466(4)
C(3)–C(4)	1.190(4)	C(4)–C(5)	1.470(4)
C(5)–C(6)	1.543(4)	C(6)–C(7)	1.510(4)
C(6)–C(11)	1.522(4)	C(7)–C(8)	1.509(4)
C(8)–C(9)	1.528(4)	C(9)–C(10)	1.539(4)
C(1)–O(2)–C(2)	114.7(2)	O(1)–C(1)–O(2)	122.8(2)
O(1)–C(1)–C(10)	125.9(2)	O(2)–C(1)–C(10)	111.2(2)
O(2)–C(2)–C(3)	107.3(2)	C(2)–C(3)–C(4)	171.0(3)
C(3)–C(4)–C(5)	177.0(3)	C(4)–C(5)–C(6)	114.1(2)
C(5)–C(6)–C(7)	108.9(2)	C(5)–C(6)–C(11)	109.3(2)
C(7)–C(6)–C(11)	112.7(2)	O(3)–C(7)–C(6)	121.1(2)
O(3)–C(7)–C(8)	121.3(2)	C(6)–C(7)–C(8)	117.6(2)
C(7)–C(8)–C(9)	113.9(2)	C(8)–C(9)–C(10)	113.0(2)
C(1)–C(10)–C(9)	109.1(2)		

Table 4

Crystal data and data collection parameters for $C_{22}H_{28}O_6$ (**44**)

Formula	$C_{22}H_{28}O_6$
FW	388.46
Color and habit	Colorless needles
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	5.283(2)
b, Å	11.659(5)
c, Å	17.877(4)
α, deg	105.51(3)
β, deg	95.98(3)
γ, deg	96.97(3)
V, Å^3	1042(6)
T, K	130
Z	2
Crystal dimensions, mm	$0.23 \times 0.17 \times 0.28$
d_{calcd}, g cm^{-3}	1.24
Radiation, (Å)	Mo-K_α, ($\lambda = 0.71069$)
μ(Mo-K_α), cm^{-1}	0.83
Range of transmission factors	0.98–0.99
Diffractometer	$P2_1$, graphite monochromator
Scan method	ω, 1.1° range, 1.0° offset for background
Scan speed, deg min^{-1}	10.0
2θ range, deg	0–47
Octants collected	h, ±k, ±l
No. data collected	3072
No. unique data	3072 [R(merge) = 0.005]
No. data used in refinement	1767 [$I > 2\sigma(I)$]
No. parameters refined	260
R	0.072
R_w	0.051 [$w = (\sigma^2(F_o)^{-1}$]

X-ray crystal structure determination for 7,18-dimethyl-1,12-dioxacyclodocosa-9,20-diyne-2,6,13,17-tetraone (44). Crystals were air-stable colorless needles. One with dimensions 0.23 × 0.17 × 0.28 mm was mounted and data collected at 130 K in a stream of dinitrogen. The triclinic space group $P\bar{1}$ was established and data collected on a Syntex $P2_1$ diffractometer (see Table 4 for complete crystal data and data collection parameters). Data for 3072 reflections were obtained using an ω scan with a scan speed of 10 deg min^{-1}, with a 1.1 deg scan width and 1 deg offset backgrounds in the range $2\theta < 47°$. The structure was solved by direct methods [35,36]. There are two half molecules of the formula unit in the asymmetric unit. The two molecules differ considerably in their conformations. There is disorder in the position of the methyl group on one of the two rings. By refinement of the occupancies of the alternative carbon positions, it was determined that they are present in a ratio of 0.79/0.21. The major carbon (C(18)) was refined anisotropically and with its hydrogen atoms at calculated positions. The minor form (C(18b)) was refined with an isotropic thermal parameter and no hydrogen atoms. The remaining non-hydrogen atoms were assigned anisotropic thermal parameters in

Table 5

Atomic coordinates (×10^4) and isotropic thermal parameters (Å^2 ×10^3) for $C_{22}H_{28}O_6$ (44)

	x	y	z	U [a]
O(1)	6355(6)	8821(3)	6204(2)	48(2)
O(2)	6808(7)	6917(3)	3185(2)	44(2)
O(3)	10428(6)	8952(3)	5943(2)	37(1)
C(1)	8209(9)	9372(4)	6049(3)	32(2)
C(2)	8359(9)	10601(4)	5929(3)	42(2)
C(3)	6287(9)	11303(4)	6267(3)	35(2)
C(4)	3416(9)	7488(4)	3901(3)	38(2)
C(5)	5141(10)	6643(4)	3547(3)	37(2)
C(6)	4682(11)	5393(4)	3682(3)	54(3)
C(7)	3590(11)	4461(4)	2910(3)	50(2)
C(8)	6935(11)	5113(4)	4072(3)	71(3)
C(9)	8166(10)	6055(4)	4811(3)	50(2)
C(10)	9132(9)	6825(4)	5355(3)	37(2)
C(11)	10486(9)	7762(4)	6037(3)	41(2)
O(4)	8213(7)	2231(3)	2132(2)	52(2)
O(5)	1801(6)	−3401(3)	241(2)	52(2)
O(6)	5396(6)	655(3)	1370(2)	36(1)
C(12)	7433(10)	1534(4)	1500(3)	38(2)
C(13)	8570(9)	1527(4)	768(3)	36(2)
C(14)	10777(9)	2565(4)	903(3)	41(2)
C(15)	−1895(9)	−2638(4)	−170(3)	45(2)
C(16)	−251(10)	−3111(4)	388(3)	40(2)
C(17)	−1303(10)	−3241(4)	1128(3)	45(2)
C(18)	392(14)	−3751(6)	1580(4)	52(3)
C(18b)	−3236(41)	−4343(18)	1049(12)	30(6) [b]
C(19)	−1984(9)	−2033(4)	1592(3)	44(2)
C(20)	196(10)	−1041(4)	1765(3)	37(2)
C(21)	2029(10)	−310(4)	1869(3)	37(2)
C(22)	4328(9)	615(4)	2079(3)	38(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. [b] C(18) and C(18b) are present in the ratio of 0.79/0.21.

Table 6

Bond lengths (Å) and bond angles (°) for $C_{22}H_{28}O_6$ (44)

O(1)–C(1)	1.203(6)	O(2)–C(5)	1.207(7)
O(3)–C(1)	1.337(6)	O(3)–C(11)	1.445(6)
C(1)–C(2)	1.498(7)	C(2)–C(3)	1.525(7)
C(3)–C(4)′	1.511(7)	C(4)–C(5)	1.485(7)
C(5)–C(6)	1.535(8)	C(6)–C(7)	1.516(6)
C(6)–C(8)	1.433(8)	C(8)–C(9)	1.498(6)
C(9)–C(10)	1.155(6)	C(10)–C(11)	1.451(5)
O(4)–C(12)	1.198(5)	O(5)–C(16)	1.208(6)
O(6)–C(12)	1.347(6)	O(6)–C(22)	1.448(6)
C(12)–C(13)	1.495(7)	C(13)–C(14)	1.525(6)
C(14)–C(15)″	1.510(7)	C(15)–C(16)	1.512(8)
C(16)–C(17)	1.524(8)	C(17)–C(18)	1.430(9)
C(17)–C(18b)	1.506(21)	C(17)–C(19)	1.537(6)
C(19)–C(20)	1.474(6)	C(20)–C(21)	1.173(7)
C(21)–C(22)	1.466(6)		
C(1)–O(3)–C(11)	114.9(4)	O(1)–C(1)–O(3)	124.1(5)
O(1)–C(1)–C(2)	125.6(5)	O(3)–C(1)–C(2)	110.3(4)
C(1)–C(2)–C(3)	113.9(4)	C(2)–C(3)–C(4)′	109.4(4)
C(5)–C(4)–C(3)′	116.3(4)	O(2)–C(5)–C(4)	122.8(5)
O(2)–C(5)–C(6)	122.0(5)	C(4)–C(5)–C(6)	115.3(5)
C(5)–C(6)–C(7)	109.3(4)	C(5)–C(6)–C(8)	112.4(4)
C(7)–C(6)–C(8)	113.5(4)	C(6)–C(8)–C(9)	114.9(4)
C(8)–C(9)–C(10)	176.2(6)	C(9)–C(10)–C(11)	176.6(6)
O(3)–C(11)–C(10)	112.0(4)	C(12)–O(6)–C(22)	112.9(3)
O(4)–C(12)–O(6)	123.2(5)	O(4)–C(12)–C(13)	124.8(4)
O(6)–C(12)–C(13)	111.9(3)	C(12)–C(13)–C(14)	112.0(3)
C(13)–C(14)–C(15)″	114.0(3)	C(16)–C(15)–C(14)″	115.1(4)
O(5)–C(16)–C(15)	120.9(5)	O(5)–C(16)–C(17)	121.3(5)
C(15)–C(16)–C(17)	117.8(4)	C(16)–C(17)–C(18)	111.7(5)
C(16)–C(17)–C(18b)	117.3(9)	C(16)–C(17)–C(19)	110.1(4)
C(18)–C(17)–C(19)	113.8(4)	C(18b)–C(17)–C(19)	116.1(9)
C(17)–C(19)–C(20)	112.4(4)	C(19)–C(20)–C(21)	175.1(5)
C(20)–C(21)–C(22)	174.6(5)	O(6)–C(22)–C(21)	108.7(3)

Symmetry code: ′ = 1 − x, 2 − y, 1 − z; ″ = 1 − x, − y, − z

the final cycles of refinement. Hydrogen atoms were included at calculated positions using a riding model, with C–H of 0.96 Å and $U_H = 1.2\ U^*_C$. The largest feature on a final difference map was 0.54 e Å^{-3} in height, 1.25 Å from C(6), and probably corresponds to a very small amount of disorder like that at C(18). The largest shift in the final cycle of refinement was 0.018 for U_{22} of C(6). Final $R = \Sigma \| F_o | - | F_c \| / | F_o | = 0.072$ and $R_w = \Sigma \| F_o | - | F_c \| w^{1/2} / \Sigma | F_o w^{1/2} | = 0.051$, with $w = (\sigma^2(F_o))^{-1}$.

Atomic coordinates are given in Table 5 and bond distances and angles in Table 6.

Acknowledgments

We thank the National Institutes of Health (Grant GM 26294) and the Chevron Research Corporation for their support of this research.

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