Journal of Organometallic Chemistry, 272 (1984) 435–446
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTION OF DICOBALT OCTACARBONYL WITH ACETYLENE AND CARBON MONOXIDE AT LOW TEMPERATURE AND PRESSURE: FORMATION OF CYCLIC ENONE PRODUCTS

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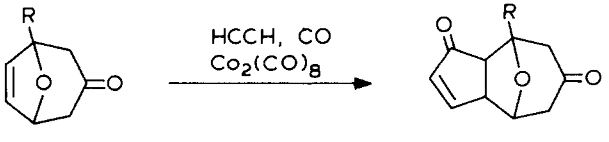
(Received March 6th, 1984)

Summary

Dicobalt octacarbonyl is shown to react with acetylene and carbon monoxide under mild conditions in dimethoxyethane or benzene to produce, in low yields, bicyclo[3.3.0]octa-3,7-diene-2,6-dione, benzoquinone, and the cyclopentadienone-derived products 3a,4,7,7a-tetrahydro-2,7-methanoindene-1,10-dione, 1-indanone, tetracyclo[5.5.2.$0^{2,6}0^{8,12}$]tetradeca-4,10,13-triene-3,9-dione, and tetracyclo-[5.5.2.$0^{2,6}0^{8,12}$]tetradeca-4,9,13-triene-3,11-dione. Possible mechanisms for the formation of these products are discussed.

Introduction

Recently our group has been studying the synthesis of cyclopentenone derivatives via the dicobalt octacarbonyl mediated reaction of strained olefins with acetylene and carbon monoxide [1]. This reaction, developed by Khand and Pauson [2], gives highly functionalized cyclopentenone derivatives, providing a convenient entry into a variety of ring systems [3] (eq. 1, 2).



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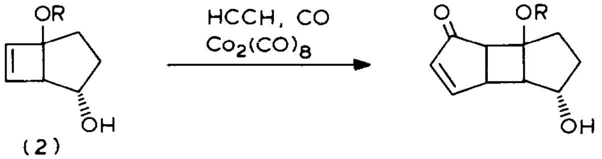

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* Camille and Henry Dreyfus Teacher-Scholar, 1981–85.

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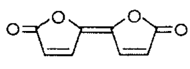
While attempting this reaction on a hindered, trisubstituted olefin, we isolated several organic products which were derived solely from the combination of acetylene and carbon monoxide in several ratios, under surprisingly mild conditions of temperature and pressure. We chose therefore to briefly investigate the organic products formed from the reaction of $Co_2(CO)_8$ with just acetylene and CO; we now report the results of these studies.

Results and discussion

The reaction of acetylenes and CO with transition metals has been reviewed [4]. With $Co_2(CO)_8$ at high temperatures under elevated CO pressures lactones **3** and **4** are produced [5]. In the absence of CO the formation of mainly 1,2,4-trisubstituted benzenes predominates [4]. The mechanism for $Co_2(CO)_8$-catalyzed acetylene trimerization has been described as proceeding via complexes **5**, **6**, and **7** [6,7]. Under our conditions benzene forms, but the lactones do not. We focus here exclusively on ketonic products formed in addition to benzene.



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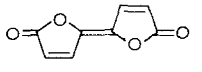

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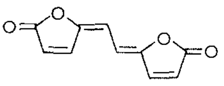

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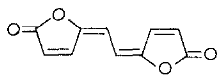

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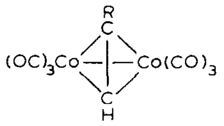

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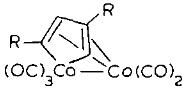

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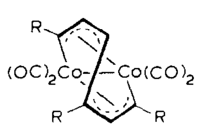

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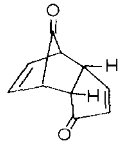


(8)

In order to determine the identity of these products, a 0.1 *M* solution of $Co_2(CO)_8$ in DME was stirred at 65 °C for five days under 1 atm of a 1/1 mixture of CO and acetylene.

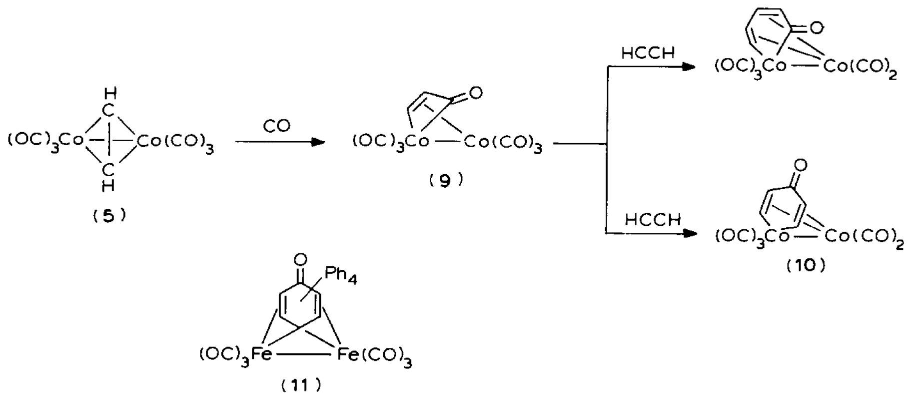
The major product, isolated in 10% yield based on the amount of $Co_2(CO)_8$ initially present (see Table 1), showed IR ν(CO) stretches at 1770 and 1690 cm^{-1}. Proton NMR signals at δ 7.38 and 6.35 ppm were consistent with, respectively, the β

TABLE 1

ORGANIC COMPOUNDS FROM THE REACTION OF $Co_2(CO)_8$ WITH ACETYLENE AND CO

Product	In DME			In C_6H_6		
	Weight (g)	Yield (%) [b]	Yield (%) [c]	Weight (g)	Yield (%) [b]	Yield (%) [c]
8	0.221	10	51	0.069	3	19
Benzoquinone	0.016	1	3	0.003	< 1	< 1
12	0.004	< 1	1	< 0.001	< 1	< 1
15	0.004	< 1	1	0.168	9	46
17	0.016	1	4	0.051	2	14
18	0.012	1	3	0.051	2	14

[a] Yields determined by NMR. [b] Mole %, based on $Co_2(CO)_8$. [c] Weight %, based on nonvolatile organic products isolated.

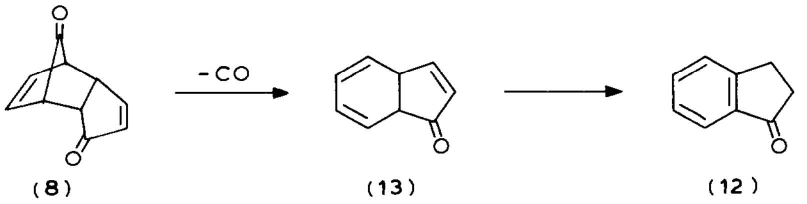


SCHEME 1

and α protons of a cyclopentenone. This compound was readily identified as 3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (**8**) by comparison of these IR and ^{1}H NMR spectra with literature data [8]. Compound **8** presumably results from a dimerization of cyclopentadienone [9] which we assume is a primary organic product in this system. Although substituted cyclopentadienones have been observed as products in several Co-catalyzed reactions of the corresponding alkynes [10,11], the reaction with $Co_2(CO)_8$ in the parent system appears not to have been reported. These cyclopentadienones are presumed to arise from intermediate **6** via insertion of CO followed by reductive elimination. An alternative pathway would involve initial insertion of CO into **5** followed by reaction with acetylene in either of two ways (Scheme 1).

The diiron complex **11** corresponding to **10** has in fact been isolated from the reaction of $Fe_3(CO)_{12}$ with diphenylacetylene [12], lending support to this possible pathway.

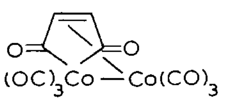
Small amounts ($<$ 1%) of 1-indanone **12** have also been isolated from the reaction of acetylene and CO with $Co_2(CO)_8$. The 1-indanone is probably formed as a secondary product from **8** via decarbonylation to dihydroindenone **13** and subsequent aromatization (eq. 3). By way of support of this assumption, Pauson has



(3)

found that $Co_2(CO)_8$ is an effective olefin isomerization catalyst, capable of converting 1,4-cyclohexadiene to 1,3-cyclohexadiene [13a]. The sequence **8** → **12** has also been effected using either $Fe(CO)_5$ or $Fe_2(CO)_9$ [14]. Further evidence for the key role played by cyclopentadienone formation in this system is provided by the isolation of two additional higher molecular weight products (vide infra).

Benzoquinone and hydroquinone have also been isolated from our reaction system, the former in about 1% yield, and the latter in trace amounts. The formation of the former is consistent with known chemistry involving several metal systems [15] and may be readily envisioned as proceeding via complexes **9** and **10** (Scheme 1). Alternatively, a second insertion of CO into **9** would give the maleylcobalt complex **14** [16], which could then go on to product.



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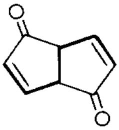

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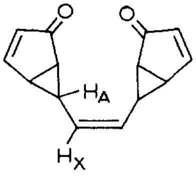
The formation of hydroquinone during the reaction may be due to the adventitious presence of water [17]. Thus a process involving $HCo(CO)_4$, produced by reaction of $Co_2(CO)_8$ with H_2O, could explain the appearance of this product. Alternatively, benzoquinone is quite a reasonable oxidizing agent ($E° = -0.711$), and may be capable of oxidation of cobalt(0) in any of a number of suitable environments (e.g. **5**, **6**, etc).

A more intriguing compound isolated from the reaction mixture gives an ^1H NMR spectrum with signals at δ 7.65, 6.07, and 3.68 ppm, of equal integrated intensity and characteristic splitting patterns. These data identify the product as the known symmetrical bis-cyclopentenone **15** [18]. Formation of **15** may occur via intermediate **7**, the precursor to benzene in the acetylene trimerization process.

The six-carbon bridge between the metal centers in complex **7** can be viewed as consisting of two overlapping metallocyclopentenes. Insertion of two CO molecules into **7** followed by elimination from the complex would give **15**. Although we favor this route to **15**, it could in principle also be formed from successive additions of acetylene and CO onto a double bond of a coordinated cyclopentadienone. Although formed in only trace amounts in DME, **15** is in fact the major ketonic product when the reaction is carried out in benzene (vide infra).

The highest molecular weight organic products isolated from this reaction system, in very low yield, were a pair of compounds of similar polarity, each with a mass spectral parent ion peak at $m/e = 212$. This mass corresponds to the combination of six acetylenes with two molecules of CO. The ^1H NMR spectrum of the slightly less polar compound displays signals at δ 7.45 (ddd, $J = 5.9$, 2.6, and 0.6 Hz), 6.16 (dd, $J = 5.9$, 1.9 Hz), 5.71 (m), 3.23 (m), and 2.58 (dd, $J = 5.9$, 3.3 Hz) ppm, all of equal integrated intensity. The signals at δ 7.45 and 6.16 ppm indicated the presence of a cyclopentenone moiety. Analysis of the spin–spin splitting [19] for the remaining multiplet in the olefinic region showed it to correspond to the XX′ part of an AA′XX′ pattern for a *cis*-1,2-disubstituted olefin with coupling constants $J_{XX'} = 8.3$ Hz, $J_{AX} = 6.4$ Hz, $J_{AX'} = 1.4$ Hz, and $J_{AA'} = 0$ Hz. Decoupling experiments revealed that the H_A protons (δ 3.23 ppm) were also coupled with the aliphatic protons at δ 3.13 and 2.56 ppm. Structures **16** and **17** were consistent with these data.



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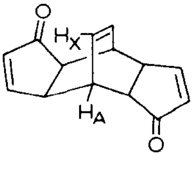


(17)

The relatively low field positions of the aliphatic proton signals, and the absence of a cyclopropyl ν(C–H) stretch in the IR, as well as plausible mechanistic arguments suggested that structure **17** was the more likely one. Owing to the ambiguity of this structural assignment on the basis of spectral data alone, however, an X-ray crystallographic study was undertaken.

Crystals of **17** grown from CH_2Cl_2/CCl_4 are triclinic, space group $P\bar{1}$, with $a = 6.321(7)$, $b = 7.39(2)$, $c = 11.14(2)$ Å, $\alpha = 103.6(2)°$, $\beta = 99.7(1)°$, and $\gamma = 91.6(2)°$, $Z = 2$. As described in the experimental section, the crystals were of poor quality, and the R index at the end of refinement (0.19) is higher than usual. Higher-quality crystals were not available, however, and no further attempt to

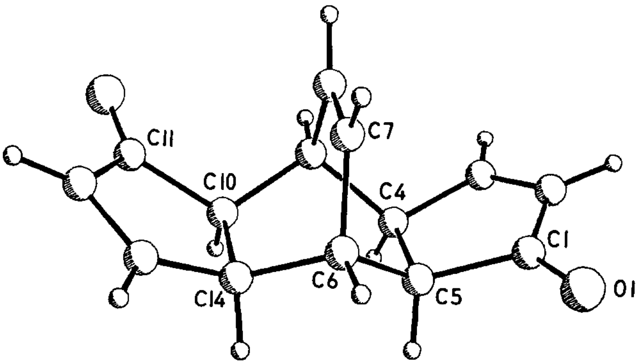
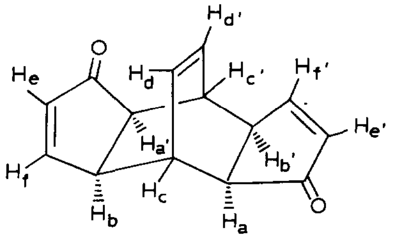


Fig. 1. Computer-generated representation of 17.

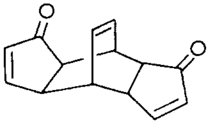
TABLE 2

PROTON NMR SHIFTS AND COUPLING CONSTANTS FOR *exo,exo*-TETRACYCLO[5.5.2.0^{2,6}.0^{8,12}]TETRADECA-4,10,13-TRIENE-3,9-DIONE (17) (From decoupled 360 MHz spectrum in $CDCl_3$. Chemical shifts relative to TMS)



Chemical shift δ (ppm)	Assignment	Appearance	J, Hz couplings
7.45	H^f	ddd	$J_{ef} = 5.9$, $J_{bf} = 2.6$, $J_{cf} = 0.6$ Hz
6.16	H^e	dd	$J_{ef} = 5.9$, $J_{be} = 1.9$ Hz
5.71	H^d	m	$J_{dd'} = 8.3^a$, $J_{cd} = 6.4^a$, $J_{c'd} = 1.4$ Hz^a
3.23	H^c	m	$J_{cd} = 6.4$, $J_{cd'} = 1.4$, $J_{bc} = 2.4^b$, $J_{ac} = 3.3$ Hz
3.13	H^b	m	$J_{bf} = 2.6$, $J_{be} = 1.9$, $J_{bc} = 2.4^b$, $J_{ab} = 5.9$ Hz
2.58	H^a	dd	$J_{ac} = 3.3$, $J_{ab'} = 5.9$ Hz

[a] Spin–spin splittings calculated [19] for AA′XX′ pattern, assuming $J_{cc'} = 0$ Hz. [b] Interpolated from width of multiplet minus known couplings.



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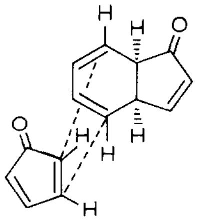


(19)

improve the refinement was made since the structure obtained is unequivocal, and serves the required purpose: establish connectivity, regiochemistry and stereochemistry. A representation of the molecule is given in Fig. 1. A complete ^{1}H NMR analysis, consistent with structure **17**, is shown in Table 2.

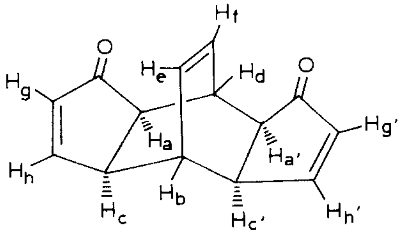
The slightly more polar compound of molecular weight 212 recovered from the reaction mixture displayed NMR signals very similar to those of compound **17**. Peaks at δ 7.44 (ddd, $J = 5.7$, 2.6, 0.8 Hz, 2H) and 6.16 (dd, $J = 5.7$, 1.8 Hz, 2H) were consistent, again, with the presence of two identical cyclopentenone rings. Multiplets at δ 5.82 (1H), 5.60 (1H), 3.49 (1H), 3.19 (2H), and 2.97 ppm, and a doublet of doublets at δ 2.52 ($J = 5.9$, 3.3 Hz) were also present. These data were consistent with structure **18**, the *syn*-counterpart to diketone **17**. The major couplings, determined by decoupling experiments are shown in Table 3.

Although direct formation of **17** and **18** on the metal center cannot be ruled out, they most likely arise via secondary reactions of cyclopentadienone in solution. Possible pathways for their formation are shown in Scheme 2.

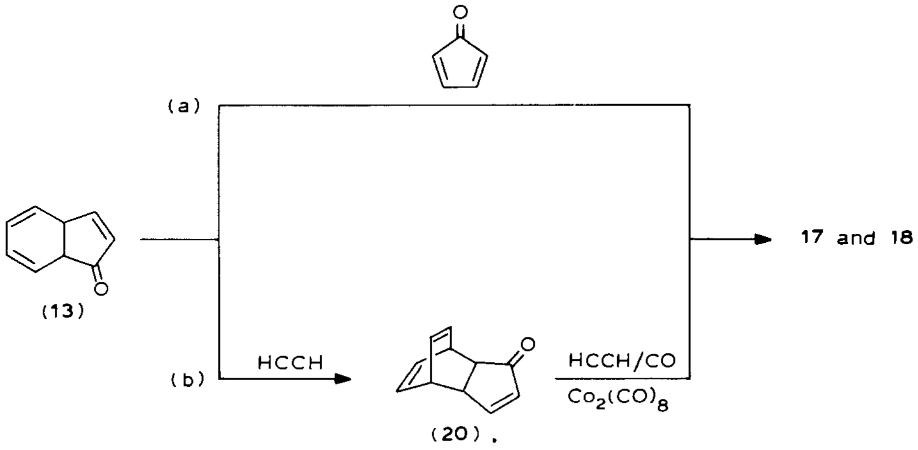
The dihydroindenone **13**, from thermal decarbonylation of **8**, may act as a diene

TABLE 3

PROTON NMR SHIFTS AND COUPLING CONSTANTS FOR *exo,exo*-TETRACYCLO[5.5.2.0^{2,6}.0^{8,12}]TETRADECA-4,9,13-TRIENE-3,11-DIONE (**18**)

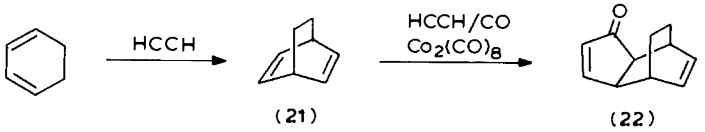


Chemical shift δ (ppm)	Assignment	Appearance	J(Hz) splittings
7.44	H^h	ddd	$J_{gh} = 5.7$, $J_{ch} = 2.6$, $J_{bh} = 0.8$ Hz
6.16	H^g	dd	$J_{gh} = 5.7$, $J_{cg} = 1.8$ Hz
5.82	H^f	m	$J_{ef} = 8.0$, $J_{fd} = 6.4$, $J_{fb} = 1.2$ Hz
5.60	H^e	m	$J_{ef} = 8.0$, $J_{eb} = 6.6$, $J_{ed} = 1.3$ Hz
3.49	H^d	m	$J_{df} = 6.4$, $J_{ad} = 3.3$, $J_{de} = 1.3$ Hz
3.19	H^c	m	$J_{ac} = 5.9$, $J_{bc} = 2$ 7, $J_{ch} = 2.6$, $J_{cg} = 1.8$ Hz
2.97	H^b	m	$J_{be} = 6.6$, $J_{bc} = 2.7$, $J_{bf} = 1.2$, $J_{bh} = 0.8$ Hz
2.52	H^a	dd	$J_{ac} = 5.9$, $J_{ad} = 3.3$Hz



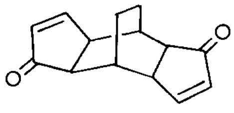
SCHEME 2

in a Diels–Alder cycloaddition with a double bond of cyclopentadienone (pathway a). Compounds **17** and **18**, produced in approximately a 1/1 ratio, are the products that would be expected from the usual endo transition states (e.g. **19**), involving attack from the less hindered side of diene **13**. This pathway is consistent with the well-known ability of cyclopentadienone to act as a normal dienophile in reactions with a variety of dienes [8]. In another conceivable route to **17** and **18**, compound **13** may undergo an initial Diels–Alder cycloaddition with acetylene to give the tricyclic trienone **20** (pathway b). Khand and Pauson [13] have reported the interesting Diels–Alder cyclization of 1,3-cyclohexadiene with acetylene under mild conditions in the presence of acetylene dicobalthexacarbonyl (**5**) to give bicyclo[2.2.2]octadiene (**21**) (eq. 4). This compound was not isolated, undergoing immediate cyclization with



(4)

additional acetylene and CO under the reaction conditions to give the isomer of **22** shown. In a similar way, if **20** is formed in our system it might be expected to undergo rapid cyclization to give both **17** and **18**. Khand and Pauson did in fact also observe mass spectrometric evidence for an otherwise uncharacterized isomer of dione **23**.



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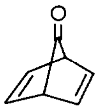
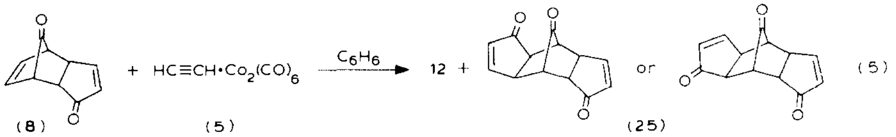


(24)

One further compound that might be expected to form in this system is 7-keto-norbornadiene (bicyclo[2.2.1]hepta-2,5-diene-7-one) (**24**), via Diels–Alder reaction of cyclopentadienone and acetylene. It has been established, however, that **24** decarbonylates even at low temperature to give benzene, and would not be observable under our experimental conditions [20].

In order to briefly study the effects of the solvent on the reaction of $Co_2(CO)_8$ with acetylene and CO, a limited number of experiments were also carried out in isooctane, and in benzene. In isooctane, under the same reaction conditions as observed above, only traces of ketonic material are produced. In benzene, however, signficant quantities of organic products are observed. The bicyclic dione **15** becomes a major product (9% based on $Co_2(CO)_8$), along with benzoquinone and cyclopentadienone dimer **8**. This increase in the yield of **15** relative to the other products may be due to a lesser tendency for CO insertions to occur in a the less strongly coordinating solvent, thus permitting up to three acetylene molecules to complex to the metal centers before migratory insertion takes place. The failure to observe significant amounts of ketonic products in isooctane is likely due to an even further reduced tendency for CO insertions, resulting almost exclusively in the formation of benzene via acetylene trimerization.

In an attempt to sort out some of the mechanistic possibilities under consideration here we carried out an experiment in which **8** was resubmitted to cycloaddition reaction conditions, in benzene solvent. The major product is a dienone system tentatively identified as one of the two regioisomers derived from further cycloaddition of acetylene and CO to **8** (eq. 5). Indanone (**12**) is formed, but **15**, **17**, and **18** are not. No **8** is present at the completion of the experiment.



Obviously we hoped to generate **13** in situ in order to test whether it is a precursor to **17** and **18** (Scheme 2). Instead, rapid, direct reaction of **8** with **5** occurs as shown, to the exclusion of simple acetylene/CO cycloaddition chemistry. Note that the absence of **25** in the earlier simple acetylene/CO experiments strongly suggests that appreciable quantities of **8** are not formed until after all the original complex **5** has been consumed. The formation of indanone in eq. 5 implies that **13** is present in this system under conditions in which pathway b of Scheme 2 might be expected to occur (i.e., **5** is present). Thus the failure of this reaction to generate **17** or **18** suggests that pathway b is inoperative. The result therefore points to pathway a of Scheme 2 as a more likely source of **17** and **18**. Unfortunately, since **5** is directly consumed by **8** in this reaction, little cyclopentadienone is expected to be present at any time; thus the experiment is ultimately incapable of positively confirming the pathway a mechanism. Since neither **13** nor any of the other proposed reaction intermediates is sufficiently stable to allow further experiments of this type, we have been unable to further pursue the mechanistic questions raised in this study at this time.

In summary, $Co_2(CO)_8$ reacts with acetylene and CO under mild conditions to produce benzoquinone, bicyclo[3.3.0]octa-3,6-diene-2,8-dione, and cyclopentadienone-derived products, further illustrating the wide range of organic transformations of unsaturated substrates accessible from this relatively simple reaction system.

Experimental

General. Dicobalt octacarbonyl (Pressure Chemical) was stored under N_2 at $-40\,°C$ and used as received. Solvents were distilled from sodium benzophenone when necessary and stored over molecular sieves. Reaction products were stored under argon. NMR spectra were recorded on Varian EM-390 and Nicolet NT-360 instruments. Decoupling experiments were performed on the NT-360 spectrometer. IR spectra were obtained on Beckman IR8 and Perkin–Elmer 180 spectrophotometers. Mass spectral data was obtained at the U.C. Davis Facility for Advanced Instrumentation. Chromatographic separations were carried out by column chromatography on silica gel (Baker) and on a chromatotron (Harrison Research; centrifugally accelerated, radial, thin-layer chromatograph) using silica gel with calcium sulfate binder (E. Merck).

Reaction of $Co_2(CO)_8$ with acetylene and carbon monoxide in DME

A solution of 5 g $Co_2(CO)_8$ in 150 ml dry, oxygen-free DME was stirred at 65 °C for five days under 1 atm of a 1/1 mixture of CO and acetylene. The purplish-brown solution gradually turned brown as the reaction progressed. The solution was cooled to room temperature, poured onto silica gel (20 g), concentrated, and placed at the top of a column containing silica gel (50 g) in hexane. Elution with hexane removed non-polar organometallic species. Elution with ethyl acetate gave crude organic products (0.408 g). Column chromatography on silica gel with 50/25/1/1, ether/dichloromethane/ethyl acetate/methanol gave four fractions with $R_f = 0.60$–0.50, $R_f = 0.50$–0.40, $R_f = 0.40$–0.20, and $R_f < 0.20$, respectively. Elution of the fraction with $R_f = 0.60$–0.50 on a chromatotron (silica gel, 50/25/1/1, ether/CH_2Cl_2/EtOAc/MeOH) gave 1-indanone (0.004 g, $R_f = 0.60$), IR (CCl_4) ν(C=O) 1700 cm^{-1}, NMR ($CDCl_3$, 360 MHz) δ 7.77 (d, $J = 7.7$ Hz), 7.58 (t, $J = 7.7$ Hz), 7.48 (d, $J = 7.0$ Hz), 7.37 (t, $J = 7.4$ Hz), 3.15 (t, $J = 5.9$ Hz), 2.69 ppm (m). Continued elution gave *p*-benzoquinone (0.016 g, $R_f = 0.57$), IR ν(C=O) 1650 cm^{-1}, NMR δ 6.7 ppm (s), and traces of hydroquinone, IR (mineral oil) ν 3350, 1510, and 1465 cm^{-1}, NMR ($CDCl_3/CH_3CN$) δ 6.7 ppm, mass spectrum m/e 110, 82, 81.

Chromatography of the material with $R_f = 0.50$–0.40 with the same solvent system gave 4,7-methano-3a,4,7,7a-tetrahydro-indene-1,10-dione (**8**, 0.221 g, $R_f = 0.45$) as white crystals m.p. 99–100 °C, IR ($CHCl_3$) ν(C=O) 1780, 1705 cm^{-1}. NMR ($CDCl_3$, 360 MHz) δ 7.38 (dd, $J = 5.6$, 2.6 Hz), 6.35 (dd, $J = 5.6$, 1.5 Hz), 6.29 (ddd, $J = 6.5$, 3.5, 0.9 Hz), 6.15 (ddd, $J = 6.5$, 3.5, 0.7 Hz), 3.51 (m), 3.38 (m), 3.19 (m), 2.90 (dd, $J = 5.7$, 5.3 Hz). Continued elution gave bicyclo[3.3.0]oct-3,7-diene-2,6-dione [18] (**15**, 0.004 g, $R_f = 0.41$), IR (CCl_4) ν 1695 cm^{-1}, NMR ($CDCl_3$, 90 MHz) δ 7.65 (d of m, $J = 5.6$ Hz), 6.07 (d of m, $J = 5.6$ Hz), 3.68 ppm (m).

Elution of the material with $R_f = 0.40$–0.20 using the same solvent system gave *exo,exo*-tetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradeca-4,10,13-triene-3,9-dione (**17**, 0.016 g, $R_f = 0.22$) IR ν(C=O) 1700 cm^{-1}, NMR ($CDCl_3$, 360 MHz) δ 7.45 (ddd, $J = 5.9$, 2.6, 0.6 Hz), 6.16 (dd, $J = 5.9$, 1.9 Hz), 5.71 (m), 3.23 (m), 3.13 (m), and 2.58 ppm (dd, $J = 5.9$, 3.3 Hz), with mass spectral peaks at m/e 212, 183, 165, 155, 141 and 131 (base peak). The structure was confirmed by a single-crystal X-ray analysis. Continued elution gave *exo,exo*-tetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradeca-4,9,13-triene-3,11-dione (**18**, 0.012 g, $R_f = 0.21$) (along with a small amount of **17**), IR ν(C=O) 1700 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 7.44 (ddd, $J = 5.7$, 2.6, 0.8 Hz, 2H), 6.16 (dd,

$J = 5.7$, 1.8 Hz, 2H, 5.82 (m, 1H), 5.60 (m, 1H), 3.49 (m, 1H), 3.19 (m, 2H), 2.97 (m, 1H) and 2.52 (dd, $J = 5.9$, 33 Hz, 2H), and mass spectral peaks at m/e 212, 184, 165, 155, 141, and 131 (base peak). High resolution mass spectrum: Found, 212.0828, calc'd for $C_{14}H_{12}O_2$, 212.0838.

The fraction of $R_f < 0.20$, along with the higher R_f fractions described above, contained unidentified organic material which did not give identifiable spectroscopic data or separate TLC spots.

*X-ray crystal structure determination for exo,exo-tetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradeca-4,10,13-triene-3,9-dione (**17**)*

A crystal with dimensions 1.5 × 0.25 × 0.04 mm was mounted and cooled to 140 K in a stream of N_2. The crystal was of poor quality, with ω scans showing multiple peaks spread over 2–3°. Data were collected on a Syntex $P2_1$ diffractometer using graphite monochromatized Cu-K_α radiation (1.5418 Å). Lattice parameters are given in the Results section. Data for 1344 reflections were obtained using an ω scan technique at a scan speed of 58.6 deg min^{-1}, with a 3 deg scan width and 2.5 deg background offsets [21] in the range $2\theta < 140°$. The structure was solved with direct methods [22]. Using 700 reflections with $I > 3\sigma(I)$, blocked-cascade least-squares refinement of 16 anisotropic non-hydrogen atoms and 14 hydrogens in calculated positions with fixed geometry (145 parameters) led to final $R = 0.186$ and $R_w = 0.177$.

Reaction of $Co_2(CO)_8$ with acetylene and CO in isooctane

A solution of 5.0 g $Co_2(CO)_8$ in 150 ml isooctane was stirred at 65 °C for five days under 1 atm of a 1/1 mixture of acetylene and CO. The crude reaction mixture was poured onto silica gel (20 g), concentrated, and placed at the top of a column containing silica gel (30 g). Elution with hexane then ethyl acetate gave only traces of ketonic organic products.

Reaction of $Co_2(CO)_8$ with acetylene and CO in benzene

A solution of 5.0 g $Co_2(CO)_8$ in 150 ml dry, oxygen-free benzene was stirred at 65 °C for five days under 1 atm of a 1/1 mixture of acetylene and CO. A total of 0.365 g nonvolatile organic material was isolated. Complete work-up as described above for the reaction in DME gave the products listed in Table 1.

*Reaction of **8** with $Co_2(CO)_8$, acetylene, and CO in benzene*

A solution of 5.0 g $Co_2(CO)_8$ and 0.25 g dione **8** in 150 ml benzene was stirred at 65 °C for five days under 1 atm of a 1/1 mixture of acetylene and CO. A total of 0.316 g nonvolatile organic material was isolated. Indanone was identified by TLC, and a new product with $R_f = 0.22$ (0.47 g) was tentatively identified as **25** (see text, eq. 5) by means of the following spectroscopic data: IR ($CHCl_3$) ν(C=O) 1775, 1700 cm^{-1}. NMR ($CDCl_3$, 60 and 500 MHz) δ 7.76 (dd, $J = 2.8$, 5.7 Hz), 7.52 (dd, $J = 2.6$, 5.8 Hz), 6.59 (dd, $J = 1.4$, 5.7 Hz), 6.32 (dd, $J = 1.4$, 5.8 Hz), 3.46 (m), 2.98 (br d, $J = 6.2$ Hz), 2.86 (d, $J = 6.0$ Hz), 2.71 (app d, splitting = 5.4 Hz, 2H), 2.31 (d, $J = 6.2$ Hz).

Acknowledgment

Financial support for this research from the Committee on Research of the University of California, Davis, the Cancer Research Coordinating Committee of the

University of California, and the National Institutes of Health (Grant GM26294) is gratefully acknowledged.

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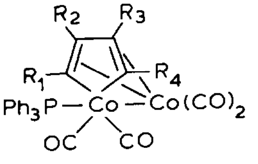

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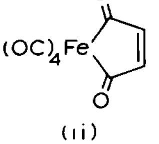

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