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ON THE REACTIVITY OF μ_2-ACETYLENES COORDINATED TO COBALT

II *. REGIOSPECIFITY OF THE CARBONYLATION OF INTERNAL ACETYLENES

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Summary

The μ_2-carbonyl- μ_2-spiro(2,3-substituted-2-butene-4-olide-4-ylidene)bis(tricarbonylcobalt)(*Co—Co*), $Co_2(CO)_7(C_4O_2R^1R^2)$, "lactone" complexes were prepared from internal acetylenes. It was found that the reaction is regiospecific; in the products from an asymmetric internal alkyne the *sp* carbon atom which had the higher value of the ^{13}C NMR chemical shift (δ) occupied the 2-, while that with the lower δ value the 3-position of the lactone ring.

Introduction

Acetylenes can be carbonylated in the presence of catalytic amounts of $Co_2(CO)_8$ in polar solvents to give bifurandiones [2—9], or with stoichiometric amounts of $Co_2(CO)_8$ in apolar solvents to give the "lactone"-complexes $Co_2(CO)_7(C_4O_2R^1R^2)$ (I) (Fig. 1) [10]; the latter are thought to be intermediates in or at least, models for catalytic carbonylation [11,12]. The formation of compounds I from terminal acetylenes at 70° C, 200—300 bar CO (in hexane solution) was shown to involve 100% regioselectivity (H = R^1) [1,12].

There are only two previous reports on the carbonylation of internal acetylenes: 2-butyne-2 was carbonylated stoichiometrically to I [10], while 3-hexyne was carbonylated catalytically to tetraethyl bifurandione [2a,8a], in

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[*] For Part I, see ref. 1. Some results of this work were presented at the Annual Meeting of the Hungarian Chemical Society (MKE Vegyészkonferencia), Aug. 23—26, 1977. Debrecen. Abstracts (Előadások összefoglalói) p. 156.

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TABLE 1

IR SPECTRA OF $Co_2(CO)_7(C_4O_2R^1R^2)$ COMPOUNDS IN THE ν(C—O) REGION [a]

Substituent		ν(C—O) stretching frequencies (cm^{-1}) [b]									
R^1	R^2	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν^{13} C—O	bridge	organic	$\bar{\nu}_t^c$
Me	Me	2109.5w	2075vs	2059.5w	2048.9vs	2037.8w	2031.1m	1994.4vw 2004.2vw 2017.0vw	1843.0s	1771.8m	2060.3
Me	Et	2109.6w	2075.4vs	2059.9w	2049.0vs	2037.6vs	2031.7m	1993.1vw 2004.8vw 2016.2vw(sh)	1843.5s	1772.5m	2059.9
Me	n-Pr	2108.5w	2074.7vs	2058.9w	2048.1vs	2030.7vs	2030.7m	1993.5vw 2004.0vw 2017vw(sh)	1842.1s	1768.7m	2059.7
Me	n-C_5H_{11}	2108.9w	2073.8vs	2058.1w	2048.1vs	2036.4vs	2029.5m	1993.2vw 2004.3vw 2015.0vw(sh)	1842.0s	1770.0m	2059.1
Et	Et	2108.1w	2074.0vs	2058.6w	2047.8vs	2036.7vs	2030.4m	1993.5vw 2005.0vw 2015.0vw(sh)	1839.5s	1767.3m	2059.3
n-Pr	n-Pr	2108.2w	2072.5vs	2058.4w	2047.6vs	2038.5vs	2031.2m	1993.5vw 2004.0vw 2015.0vw(sh)	1841.0s	1774.0m	2059.4

[a] In n-hexane, DCl calibration. [b] The numbering of the terminal frequencies follows the order of appearance. [c] Average terminal frequency.

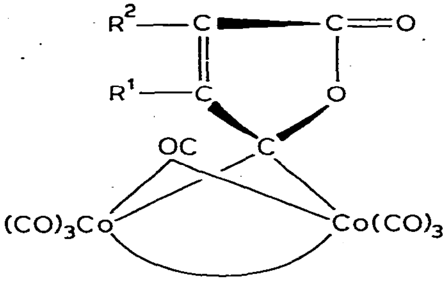

Fig. 1. $Co_2(CO)_7(C_4O_2R^1R^2)$ (I).

2.5 and 6.3% yields, respectively. We decided to extend our earlier studies on the regioselectivity of the carbonylation to that of internal acetylenes. A series of compounds I was prepared having neither R^1 and R^2 as H, and the structure of the product was investigated by spectroscopic methods.

Results and discussion

Preparation of the complexes

We found that internal alkynes ($R^1C_2R^2$) react with $Co_2(CO)_8$ in hexane solution as do terminal ones [1,10,12], but somewhat more forcing conditions (110—130°C, 300—400 bar CO, 10—40 h) are necessary to achieve 1—40% yields.

Internal acetylenes with $R^1 = R^2$ = t-Bu, Ph, substituted Ph or I and R^1 = Ph, R^2 = Me could not be carbonylated, as reported in part earlier [1], but acetylenes with $R^1 = R^2$ = alkyl were found to form compounds I. (μ_2-Acetylene)-$Co_2(CO)_6$ compounds [13] reacted in the same way as a mixture of the corresponding acetylene and $Co_2(CO)_8$.

The products were separated by preparative TLC (silica gel adsorbent, methylene chloride eluent, CO atmosphere). Compounds I from internal alkynes could be readily crystallized. All the compounds prepared in this way were reddish-orange. The isomeric purities of the compounds was checked by repeated analytical TLC, and the results indicated that only one isomer was formed.

Spectra and structure

Infrared ν(C=O), (Table 1, Fig. 2) ^{1}H NMR (Table 2) and mass spectra (Table 3) of compounds I were recorded. The spectroscopic results indicated a structure (Fig. 1), where R^1 is always the lighter R group if the starting alkyne was asymmetric. The assigned structure is based on the following spectroscopic arguments:

(i) Compounds I ($R^1, R^2 \neq$ H) show a ν(C=O) spectrum very similar in shape to that of the lactone complexes prepared from terminal alkynes [1,14]. This suggests the same overall geometry, which is analogous to that found by Mills and Robinson [15] for the $R^1 = R^2$ = H derivative.

(ii) The triplet form of the lower terminal $\nu(^{13}C{=}O)$ band system further supports this view, indicating [16] not only that the axial and equatorial carbonyl

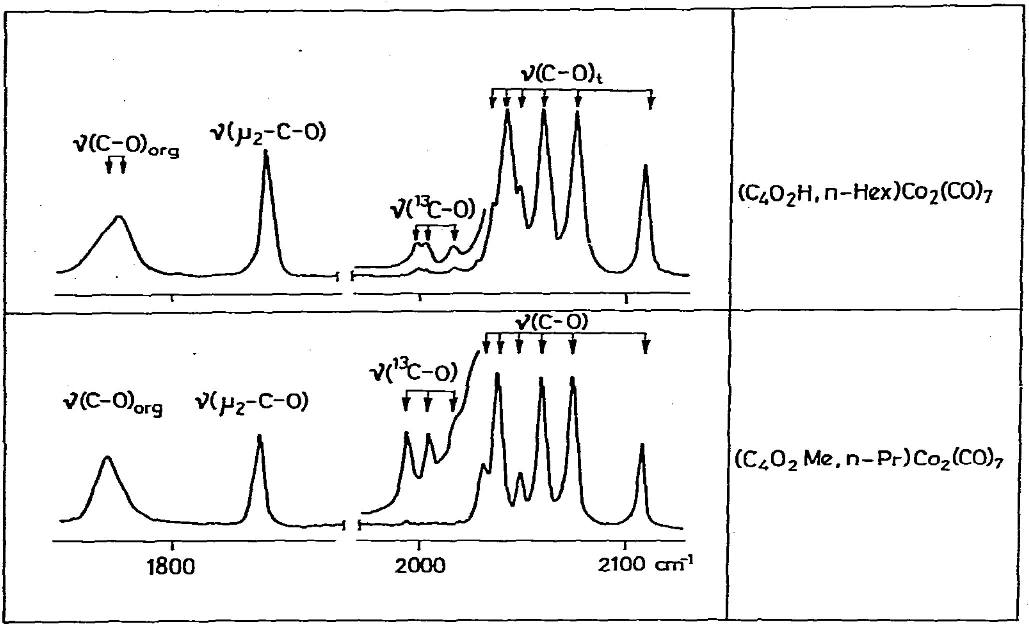

Fig. 2. IR spectra of $Co_2(CO)_7(C_4O_2Me, n\text{-}Pr)$ and $Co_2(CO)_7(C_4O_2H, n\text{-}Hex)$ in the ν(C—O) region (solvent n-hexane).

groups are different but that there are also two sets of equatorial carbonyl groups.

(iii) The position of the terminal $\bar{\nu}_t$(C=O) bands is shifted by ca. 3 cm^{-1} towards lower wave numbers (c.f. $\bar{\nu}_t$ values in Table 1 and from ref. 1). This indicates the presence of an additional electron donor substituent in the

TABLE 2

^{1}H NMR DATA FOR $Co_2(CO)_7(C_4O_2R^1R^2)$ COMPOUNDS

Substituents		Chemical shift (δ, ppm) [b]	Assignment
R^1	R^2		
H [a]	Me	1.83(s, 3 H)	2-CH$_3$
		7.30(s, 1 H)	3-H
Me	Me	1.73(s, 3 H)	2-CH$_3$
		2.00(S, 3 H)	3-CH$_3$
H [a]	n-Pr	0.96(t, 3 H)	γ-CH$_3$
		1.6(m, 2 H)	β-CH$_2$
		2.23(t, 2 H)	α-(2-)CH$_2$
		7.33(s, 1 H)	3-H
Me	Et	1.05(t, 3 H)	β-CH$_3$
		2.05(s, 3 H)	3-CH$_3$
		2.3(m, 2 H)	α-(2)-CH$_2$
Me	n-Pr	1.02(t, 3 H)	γ-CH$_3$
		1.61(m, 2 H)	β-CH$_2$
		2.00(s, 3 H)	3-CH$_3$
		2.3(m, 2 H)	α-(2)-CH$_2$

[a] For comparison, ref. 1. [b] CCl$_4$ solution, TMS internal standard.

TABLE 3

MASS SPECTRAL DATA FOR $Co_2(CO)_7(C_4O_2Et, Et)$

Mass of ions (m/e)	Rel. intensity (%)	Assignment
452	15	$[Co_2(CO)_7(C_4O_2Et, Et)]^+$
424	38	$[Co_2(CO)_6(C_4O_2Et, Et)]^+$
396	24	$[Co_2(CO)_5(C_4O_2Et, Et)]^+$
368	9	$[Co_2(CO)_4(C_4O_2Et, Et)]^+$
340	34	$[Co_2(CO)_3(C_4O_2Et, Et)]^+$
312	90	$[Co_2(CO)_2(C_4O_2Et, Et)]^+$
284	100	$[Co_2(CO)(C_4O_2Et, Et)]^+$
256	88	$[Co_2(C_4O_2Et, Et)]^+$
138	38	$[C_4O_2Et, Et_2]^+$
123	31	$[C_4O_2Et, CH_2]^+$
109	32	$[C_4O_2Et]^+$
94	16	$[C_4O_2CH_2]^+$
80	14	$[C_4O_2]^+$
69	95	$[C_2OEt]^+$
54	50	$[C_2OCH_2]^+$
40	31	$[C_2O]^+$

lactone ring relative to the R^1 = H series. The same effect is reflected also in the position of the bridging carbonyl absorptions.

(iv) It is well known that the Fermi resonance splitting of the organic ν(C=O) band of γ-butenolides is determined by the size of the 2-substituent as well as by the ratio of the sizes of the 2- and 3-substituents [17]. The absence of the resonance splitting of this band in the spectrum of the compounds prepared in course of this work supports the assignments of R^1 and R^2 given in Table 1.

(v) The absence of proton signals corresponding to either of the butenolido hydrogens in the 2- or 3-position [1] in the ^{1}H NMR spectrum proves that the butenolido unit in complexes I is 2,3-dialkyl substituted.

(vi) The presence of two methyl signals in the ^{1}H NMR spectrum of the "lactone" complex prepared from 2-butyne provides further evidence for the suggested structure.

(vii) The ^{1}H NMR spectrum of the key compound (I, $R^1 = R^2$ = Me) can be interpreted as follows. When the position of the two signals is compared with that of the methyl signal in the spectrum of I (R^1 = H, R^2 = Me) [1], one of the signals is shifted to lower and the other to higher field. The "second" alkyl substitution can cause only a higher field shift, and therefore the signal at δ 1.73 ppm must correspond to the methyl group in the 2-position (R^2 = Me), and the other to R^1 = Me. Since the signal corresponding to the former disappears in the spectrum of the compounds prepared from 2-alkynes, the assignment R^1 = Me, R^2 = alkyl for these derivatives seems to be correct. The same conclusion is reached on the basis of a comparison of the spectrum of I, ($R^1 = R^2$ = Me) with that of I ($R^1 = R^2$ = H) which reveals that the lower field methyl signal corresponds to the 3-Me group.

(viii) The mass-spectral fragmentation pattern of the complexes seems to follow the usual pattern of fragmentation of organo-substituted metal carbonyls [18], i.e. a stepwise loss of all carbonyl groups can be observed, then the loss of the organic (butenolide) ligand, and then fragmentation of the latter. The fragmentation of the butenolide unit starts with the loss of the alkyl groups, which is significant from the viewpoint of our structural assignment. The loss of two methyl and two methylene fragments in the mass spectrum of I (R^1 = R^2 = Et) (cf. Table 3) excludes all other structural possibilities for the organic part of the compound.

Summarizing, it can be seen that the high regioselectivity in the formation of compounds I is observed also with internal acetylenes *. At first it seemed that this effect might be exclusively due to steric factors, since the size of R^2 was always greater than that of R^1, but it seemed unlikely that steric effects so far away from the apparent reaction center would give rise to quantitative regioselectivity. Furthermore diiodoacetylene, in which the substituents while not small are not much larger than methyl groups, could not be carbonylated at all.

In searching for an experimental parameter which might give a direct guide to the chemical reactivity at the separate reaction centers (the acetylenic carbons) we looked at ^{13}C NMR spectroscopy. Thus we measured and/or obtained from the literature the ^{13}C NMR shifts for the substrates we used in the stoichiometric carbonylation reaction (Table 4). When these data are examined along with the results of the preparative experiments the following conclusions can be drawn:

(i) To be carbonylated the acetylene must contain at least one carbon atom which has ^{13}C NMR shift below than about 80 ppm. (The only exception is 1-phenylprop-1-yne, which falls only 0.2 ppm outside this range.)

(ii) It seems that a lower limit (in terms of $\delta(^{13}C)$) must also exist, since C_2I_2, which shows an extremely low δ value ** cound not be carbonylated, but we do not have enough data to define the position of this limit. (Other homo- or hetero-dihaloacetylenes would be good models, but their highly explosive nature presents problems for high-pressure work.)

(iii) The carbon atom showing the lower chemical shift forms the 3-position of the lactone ring.

(iv) It is noteworthy that the observed high regioselectivity might be associated with extension of the (π and/or π^*) orbitals on the acetylenic carbons ***.

A similar association between the regioselectivity of a transition metal-catalysed cyclization and extension of the frontier molecular orbitals was recently demonstrated [25,26].

It should be added that the proposal that isomerization of the C≡C triple bond occurs, which was based on the isolation of I (R^1 = H, R^2 = n-Hex) from the product of carbonylation of 2-octyne [27], is erroneous. Our 2-octyne sample was later shown by GLC analysis to contain 17% of 1-octyne.

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* Is should be noted that this is also the case with catalytic carbonylation, e.g. no formation of 3,6-disubstituted bifurandiones from terminal acetylenes has ever been detected.

** This is consistent with the only published value for an iodoacetylene, 1-iodohex-1-yne, viz. δ ^{13}C, TMS = —6.0 ppm for 1-C [24].

*** INDO calculations by G. Mouvier and collaborators (Paris, France) are now in progress to get a better insight into this aspect of the problem.

TABLE 4

^{13}C NMR DATA FOR ACETYLENES ($R^1C_2R^2$) STUDIED IN THE CARBONYLATIONS [c]

Acetylene		Chemical shift (ppm)		Literature for NMR data	Results of attempted preparation of complex I (% yield)
R^1	R^2	δ_1	δ_2		
H	Et	67.0	84.7	[20]	~70[23]
H	n-Pr	69.0	84.4	[a]	60[1]
H	n-Bu	67.4	82.8	[21]	89[23]
H	n-C_5H_{11}	67.4	82.9	[21]	~80[23]
H	Ph	77.7	83.3	[22]	48[1]
Me	Me	73.6	73.6	[20]	35 [b]
Me	Et	75.0	80.9	[a]	30 [b]
Me	n-Pr	73.7	76.9	[21]	10 [b]
Me	Ph	85.7	79.8	[22]	—
Et	Et	79.9	79.9	[21]	low [b]
n-Pr	n-Pr	79.0	79.0	[21]	~1 [b]
t-Bu	t-Bu	85.3	85.3	[a]	—
Ph	Ph	88.0	88.0	[a]	—
Ph	p-MeC_6H_4	88.2	87.8	[a]	—
Ph	m-MeC_6H_4	88.2	87.5	[a]	—
p-MeC_6H_4	p-MeC_6H_4	87.0	87.0	[a]	—
I	I	5.3	5.3	[a]	—

[a] Our measurement, acetone-d_6 solvent. [b] Cf. Experimental. [c] Only the signals of the *sp* carbons are tabulated, TMS reference.

Experimental

The materials used were of commercial origin, with the expection of $Co_2(CO)_8$ which was prepared by the method of Markó et al. [28].

IR spectra were recorded using an UR-20 (Carl Zeiss, Jena) spectrometer, NMR spectra with a Varian T-60 (60 MHz) spectrometer and mass spectra with a Varian-MAT 111 spectrometer. IR spectra were recorded with simultaneous DCl calibration [29].

A typical procedure for preparation of the lactone complexes from internal alkynes was as follows:

3.42 g (10 mmol) $Co_2(CO)_8$ and 50 cm^3 hexane were placed in a stainless steel rocking autoclave together with 0.82 g (10 mmol) of 2-hexyne. The autoclave was closed and *P*(CO) increased to 300 bar at room temperature. Then the autoclave was rocked for 35—40 h at 100°C. Samples were taken every 8—10 h, and the progress of the reaction was monitored by IR spectroscopy. After the IR spectra showed no further increase in the amount of the lactone complex, the autoclave was cooled to room temperature and opened, and the products were separated by column chromatography or TLC (eluted with CH_2Cl_2). The chromatographed lactone complex was further purified by two recrystallizations from Et_2O/n-hexane (1/1). Yields and analytical data are tabulated in Table 5.

The same products and yields were obtained starting from $(R^1C_2R^2)Co_2(CO)_6$ complexes.

Melting points could not be determined for compounds I because of decomposition.

TABLE 5

ANALYTICAL DATA AND YIELDS OF $Co_2(CO)_7(C_4O_2R^1R^2)$ COMPOUNDS

Substituents		Molecular weight (Found [a] (calcd.))	Co (Found(calcd.)(%))	Yield (%)
R^1	R^2			
Me	Me	424 (424.33)	28.4 (27.78)	35
Me	Et	438 (438.36)	27.5 (26.89)	30
Et	Et	452 (452.38)	*b* —	*b*
Me	n-Pr	452 (452.38)	*b* —	10
n-Pr	n-Pr	*b* (470.44)	25.3 (25.01)	1
Me	n-C_5H_{11}	*b* (470.44)	25.6 (25.01)	10

[a] Molecular weights were measured mass spectrometrically. [b] Not measured.

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