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ORGANOCOBALT COMPLEXES

VII*. THE ROLE OF BUTENOLIDE COMPLEXES IN THE COBALT-CATALYSED SYNTHESIS OF BIFURANDIONES FROM ACETYLENES AND CARBON MONOXIDE

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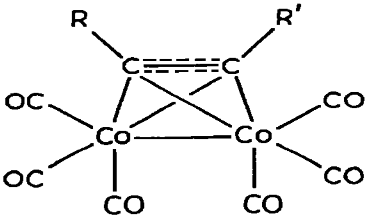
Summary

The butenolide cobalt complexes derived from monosubstituted acetylenes are shown to be substituted in the α-position of the lactone ring. Their intermediacy in the catalytic formation of 2,6-disubstituted bifurandiones is demonstrated, and shown to require addition of both free acetylene and carbon monoxide.

Introduction

Complexes with butenolactone groups acting as bridging carbene ligands were isolated [2] from the reaction of octacarbonyldicobalt with acetylenes followed by carbonylation. The first-formed hexacarbonylacetylenedicobalt complexes (I) insert three molecules of carbon monoxide in the second stage and the structure (II) of the products was fully established by single crystal X-ray diffraction studies [3].



(I)

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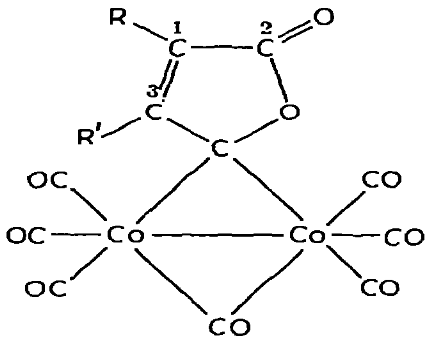
* For part VI see ref. 1.



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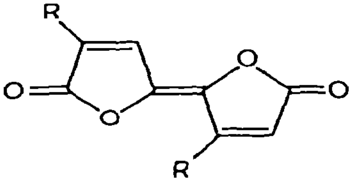

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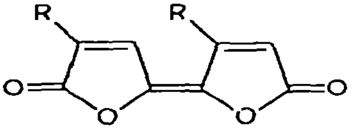

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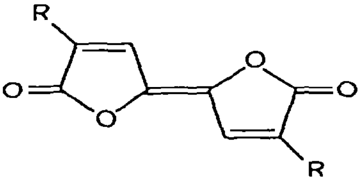


(V)

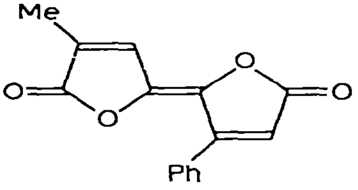
Although it has always appeared probable [2] that these butenolide complexes are intermediates in the independently-discovered [4, 5] formation of the bifurandiones III by cobalt carbonyl-catalysed reaction of acetylenes with carbon monoxide, this has never been demonstrated. We set out to do so and if possible to throw light on the steps involved. A recent report of very similar work [6] prompts us to present our results at this stage.

Discussion

Apart from a phosphine-substituted derivative [7] only the three butenolactone complexes from acetylene, 1-pentyne and 2-butyne originally described [2] are known. On the other hand acetylene, propyne, 1-butyne and four arylacetylenes were used [4] in the preparation of bifurandiones III, all reacting in moderate to good yield, while only poor conversion was achieved with 3-hexyne, the only internal alkyne examined.

Separation of the product from phenylacetylene [4] and the more detailed studies [8] of the products from propyne showed that three isomeric bifurandiones could be isolated: the *trans*-2,6-disubstituted bifurandiones III predominate (vide infra) over their *cis*-isomers (IV) and the more symmetrical *trans*-2,7-isomers (V) are relatively minor products. Now two general routes for conversion of lactone complexes II to bifurandiones III, etc., can be envisaged: the simpler pathway would require the linkage of two of the carbenoid lactone fragments, be it after liberation as carbenes or while still bonded to the metal. But this could only account for the formation of unsymmetrical bifurandiones III and IV as major products if the lactone precursor II were a mixture of two isomers (R and R' interchanged) in approximately equal proportion. Quite contrary to such a postulate, complexes II are well-crystallised products which are readily isolated and appear homogeneous. The structural evidence reported below shows that they bear the single substituent, R (R′ = H), at carbon 2 of the lactone ring as shown in structure II. As the sole precursor, such a complex could only lead to the 2,7-disubstituted bifurandione (V). We find indeed that this is formed, albeit in very low yield, on heating the complex in solution.

The route from a homogeneous precursor II (R′ = H) to the unsymmetrical bifurandiones most probably involves successive insertion of carbon monoxide, acetylene and again carbon monoxide. Indeed we find that the butenolactone complex II becomes an efficient precursor of bifurandione III (and isomers) if and only if it is heated in the presence of free acetylene under carbon monoxide pressure. Moreover, a different acetylene can be used at this stage and we have succeeded in isolating the unsymmetrical bifurandione of probable structure VI when treating the propyne-derived lactone complex II (R = Me, R′ = H) with phenylacetylene. However the inevitable formation of I (R = Ph, R′ = H) and hence II (R = Ph, R′ = H) by continuation of the catalytic cycle under the reaction conditions makes the product mixture complex and the yield of the 'mixed' product VI low. Indeed the rapid and efficient formation of lactone complexes II from acetylene complexes I and these in turn from octacarbonyldicobalt or from the tetracarbonylcobaltate ion, $Co(CO)_4^-$, makes all these cobalt compounds almost equally good precursors of the bifurandiones.



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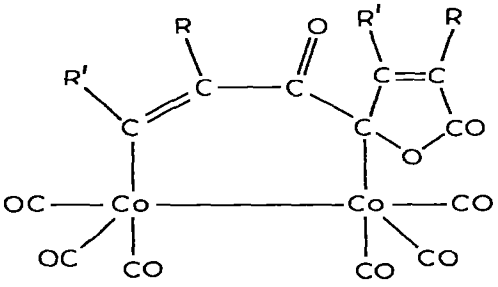

(VII)

Attempts to detect or isolate intermediates between the butenolide complex II and the metal-free product III proved unrewarding. The usual mode of preparing the former is from the acetylene complexes I under pressure of carbon monoxide. The conditions for bifurandione formation are no more severe and there is no evidence of further uptake of carbon monoxide by complexes II in the absence of acetylenes; however it may occur in a concerted process as the acetylene becomes coordinated to the metal atom. On the other hand, without carbon monoxide pressure, the acetylenes react with complexes II to yield products [2] which cannot be on the direct reaction path since they result from incorporation of usually 2 and sometimes 3 acetylene units*. These products were only partially characterised in the early work [2] and are the subject of continuing work in our laboratory. But we did not find simple products result-

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* This result, from product analysis, probably does not conflict with the observed evolution [2] of less than 2 moles of carbon monoxide as the reactions are far from clean.

ing from incorporation of a single acetylene which might be intermediates before the final CO insertion and cleavage of the organic portion from the metal atoms. We suggest therefore that an intermediate, perhaps of the type VII, is involved which reacts too fast to be isolated, either with excess acetylene or excess carbon monoxide.

Although we can confirm from our experience the much-reduced reactivity of disubstituted acetylenes in the formation of both butenolide complexes II [2, 6] and bifurandiones [4], we have repeated the use of 3-hexyne in the latter reaction and confirmed by ^{1}H NMR spectroscopy that the product is the expected tetraethyl-substituted bifurandione [4]. This contrasts with the Hungarian workers' observation [6] that 2-octyene formed a lactone complex of type II which must have resulted from 1-octyne formed by triple bond migration.

We also note that whereas the unsubstituted bifurandione III (R = H) suffers *trans* → *cis* isomerisation on warming in sulphuric acid [4], its dimethyl derivative III (R = Me) requires more severe conditions for isomerisation and apparently gives an equilibrium mixture still containing chiefly the *trans*-isomer.

Substitution pattern in complexes II

That the complexes II derived from mono-substituted acetylenes bear the substituents on carbon-2, i.e. α to the lactone carbonyl, was strongly suggested by the following ^{1}H NMR data:

Complex	R(τ)	R'(τ)	Solvent
R = R' = H	3.95 d	2.42 d	CS_2
R = CH_3, R' = H	8.2 s	2.38 s	$(CD_3)_2CO$
	8.2 s	2.74 s	$CDCl_3$
R = C_6H_5, R' = H	2.2 m, 2.9 m	2.38 s	CS_2
	2.1 m, 2.6 m	2.27 s	$CDCl_3$

It is well known that in α,β-unsaturated carbonyl systems (including lactones [9]) the α-proton resonates at higher field than the β-proton and application of this rule leads directly to the above assignment. Since, however, it could be argued that the proximity of the metal atoms might have an effect which is not readily predictable, we decided to confirm this conclusion by degradative studies.

Reductive degradation provided the desired evidence. Catalytic hydrogenation of the unsubstituted complex II (R = R' = H) has previously been reported [10] to yield a mixture of γ-butyrolactone and butyric acid. We reduced the phenyl-substituted complex II (R = Ph, R' = H) with sodium borohydride at 0° and observed smooth conversion to α-phenylbutyrolactone. Its identification (see Experimental) fully confirms the above structural assignment. No butenolactone was observed and the hydrogenation of the double bond under these conditions may result from generation of $HCo(CO)_4$, which is known to effect such reductions [11] rather than by direct reaction of the borohydride.

Oxidative degradation was also examined under conditions similar to those used [1] for complex I (R = Ph, R' = H). Ceric ammonium nitrate in ethanol converted the unsubstituted complex II (R = R' = H) chiefly to diethyl maleate, whereas the phenyl-substituted complex II (R = Ph, R' = H) gave a monoethyl ester of phenylmaleic acid.

Experimental

All reactions were carried out under nitrogen. Neutralised alumina was the adsorbent used for chromatography and light petroleum refers to the fraction of b.p. 40-60° unless otherwise stated. The unsubstituted lactone complex II (R = R' = H), m.p. 114-116°, was obtained by the published method [2] in 70% yield.

Complex II (R = Me, R' = H)

Hexacarbonylpropynedicobalt (I, R = Me, R' = H) (20 g) and light petroleum (40 ml) were placed in a 200 ml steel rocking autoclave under 210 atm. of carbon monoxide and then heated to 70° for 20 h. After cooling, the product was collected, washed with petroleum ether and recrystallised from this solvent to give red crystalline II (R = Me, R' = H) (16.4 g, 65%), m.p. 109° (dec.). [Found: C, 35.1; H, 1.4. $C_{12}H_4Co_2O_9$ calcd.: C, 35.2; H, 1.0%.]

Complex II (R = Ph, R' = H)

Hexacarbonyl(phenylacetylene)dicobalt (I, R = Ph, R' = H) (10 g) and n-hexane (25 ml) were placed under 250 atm. carbon monoxide and then heated to 75° for 20 h in a rocking autoclave. Work-up as in the preceding experiment gave II (R = Ph, R' = H) (6.5 g, 60%), m.p. 162-165°. [Found: C, 43.3; H, 1.4. $C_{17}H_6Co_2O_9$ calcd.: C, 43.25; H, 1.3%.]

Thermal decomposition of II (R = Ph, R' = H) and II (R = Me, R' = H)

Pyridine is known [2] to displace the lactone group from the complex, yielding $[Co(CO)_4]_2[Co(C_5H_5N)_6]$, but we were unable to isolate organic products from solutions of the complex in pyridine or in benzene containing pyridine. Decomposition was also examined in benzene (no decomposition after 10 h reflux), carbon tetrachloride and 1,2-dimethoxyethane. Only in the last case could the bifurandione V (R = Ph) be isolated in very low yield after reflux (1-2 h) or preferably after standing for 2 days. In this way the solution of II (R = Ph, R' = H) (0.7 g) in dimethoxyethane (30 ml) changed from the initial deep red to yellowish-brown. Filtration, evaporation and crystallisation of the residue from ether/light petroleum gave an orange-yellow solid (80 mg) whose IR and UV spectra corresponded to those of the bifurandione V (R = Ph). Mol. wt. found: 316.0730. $C_{20}H_{12}O_4$ calcd.: 316.0735.

Complex II (R = Me, R' = H) was unchanged after stirring in 1,2-dimethoxyethane for 48 h, but heating a solution (2 g in 25 ml) to 90° for 4 h yielded after purification nearly colourless crystals (5 mg) whose infrared spectrum corresponded to that reported [8] for the bifurandione V (R = Me).

Ceric oxidation of complexes II

(a) The unsubstituted complex II (R = R' = H). An ethanol solution (50 ml) of the complex (1.5 g, 4.8 mmol) was stirred for 4 h with ceric ammonium nitrate (7 g, 0.144 mol). Water (30 ml) was added and the solution extracted

TABLE 1

YIELDS OF BIFURANDIONES III-V (R = Me)

Cobalt precursor (g)	Propyne[a] (g)	Initial[b] CO pressure (atm.)	Temp. (°C)	Reaction time (h)	Solvent (ml)	Yields (g)[a]			Total (%)
						III	IV	V	
$Co_2(CO)_8$[c] (3)	10	173	100-110	2.5	$Me_2CO + Ac_2O$ (160)	1.3	0.9	0.2	
$Co_2(CO)_8$ (0.4)	2.2	180	106	3	Me_2CO (20)	0.3	0.08		7
$Co_2(CO)_8$ (0.4)	2.2	180	106	3	Me_2CO + MeOH (20) (0.5)	0.37	0.12		9
$MeC_2HCo_2(CO)_6$ (1.87)	1.62	170	100	5.5	Me_2CO (15)	0.55	0.1		17
$MeC_2HCo_2(CO)_6$ (2.4)	10	190	60	24	Me_2CO (50)	0.05	trace		
$MeC_2HCo_2(CO)_6$ (1.42)	2.8	180	100 120	5 4	Me_2CO (15)	0.94			18.5
Complex II (R = Me, R' = H) (1.0)	4.3	200	100 120	5 3	Me_2CO (15)	2.94	0.08	0.05	30
$[Co(CO)_4]_2[Copy_6]$ (0.55)	2.5	180	96	3	Me_2CO (12)	0.715	0.02		12.5

[a] Propyne was condensed into cooled solvent and increase in weight determined; loss on transfer to autoclave makes weights of propyne maximum and hence yields minimum figures. [b] Pressure before heating. [c] Ref. 8.

with a mixture of ether and light petroleum. The dried ($CaCl_2$) extract was evaporated and the residue distilled (120°/1 Torr) to yield the product (0.20 g) whose IR and ^1H NMR spectra showed it to be largely diethyl maleate by comparison with spectra of an authentic sample.

(b) The phenyl derivative II (R = Ph; R' = H). This complex (1.5 g, 3 mmol) was similarly oxidised (6 h) with ceric ammonium nitrate (4.5 g, 9 mmol), in ethanol and the diluted solution then extracted with ether/light petroleum. Evaporation of this extract yielded crystalline ethyl phenylmaleate, which formed colourless needles from pentane. τ ($CDCl_3$) 0.65 (1 H, br, OH), 2.45 (5 H, m, Ph), 2.62 (1 H, s, =CH), 5.5 (2 H, q, CH_2) and 8.6 (3 H, t, CH_3). [Found: C, 66.0, H, 5.9. $C_{12}H_{12}O_4$ calcd.: C, 65.45, H, 5.5%.]

Reduction of complex II (R = Ph, R' = H)

A suspension of the complex (3 g, 6.4 mmol) in a mixture of ether (200 ml) and ethanol (50 ml) was cooled in ice and stirred during, and for 0.5 h after, addition of an ethanol solution of sodium borohydride (2 g). Water (100 ml) was then added and stirring continued for 0.5 h. The ether layer was then separated, the aqueous layer extracted with more ether and the combined ether solutions washed with water and dried over a mixture of sodium sulphate and sodium bicarbonate. Evaporation and chromatography of the residue on silica gel using ether/light petroleum (2/1) as eluent gave two bands. A pale red band was found to contain unchanged II (R = Ph, R' = H) and the slower moving pale yellow band was eluted, evaporated and distilled at 144°/5 Torr to give 2-phenylbutyrolactone (0.66 g, 65%) as a colourless oil, τ ($CDCl_3$) 2.71 (5 H, m, Ph), 5.7 (2 H, m, H-4), 6.25 (1 H, dd, H-2) and 7.5 (2 H, m, H-3). [Found: C, 74.15; H, 6.2. $C_{10}H_{10}O_2$ calcd.: C, 74.1; H, 6.2%.]

Formation of bifurandiones

(a) The reactions with propyne were carried out in a 50 or 200 ml steel autoclave as previously described [4, 5, 8] under the conditions listed in the Table 1. The products from propyne were readily identified by comparison of their infrared spectra with the published [8] spectra.

(b) In addition, we carried out similar reactions with phenylacetylene, but did not completely separate the isomeric phenyl-substituted bifurandiones. These experiments gave results in agreement with published data [4, 5, 9] and showed that the tetracarbonylcobaltate anion as $[Co(CO)_4]_2[Co(C_5H_5N)_6]$ could efficiently replace the octacarbonyl, $Co_2(CO)_8$, as precursor, both yielding some acetylene complex I (R = Ph, R' = H) in addition to the bifurandiones. No bifurandione was formed when lactone complex II (R = Ph, R' = H) or its precursor I (R = Ph, R' = H) was heated under carbon monoxide pressure under the same reaction conditions but without added free acetylene.

(c) We further confirmed the formation [4] in much lower yield of the fully substituted bifurandione from 3-hexyne and either octacarbonyldicobalt (1.6% yield) or the complex I (R = R' = Et) (≈5%). Our product had m.p. 117° (lit. [4] 95-96°) and its ^1H NMR spectrum showed the presence of two different ethyl groups [τ (CS_2) 7.34 (q, CH_2), 7.71 (q, CH_2) and 8.86 (apparent q resulting from two overlapping t, CH_3) ratio 1/1/3] and no other protons.

(d) Formation of compound VI. The lactone complex II (R = Me, R' = H)

(1.86 g, 4.8 mmol) was added to a chilled solution of phenylacetylene (1.1 ml, 10 mmol) in acetone (15 ml) in a 50 ml stainless steel autoclave which was quickly pressurised to 200 atm. with carbon monoxide. The autoclave was rocked for 3 h at room temperature and then for a further 4 h at 100°. After cooling the solvent was removed in vacuo and the residue extracted with 800 ml of boiling light petroleum. The extract was cooled to —60°, depositing phenyl-substituted lactone complex II (R = Ph, R' = H) (0.62 g, 1.4 mmol). Further extraction of the residue with boiling benzene, clarification of the extract with a little charcoal, filtration and evaporation gave an orange solid (0.40 g) which was dissolved in acetone and allowed to crystallise fractionally by slow evaporation to give the bifurandione VI (70 mg, 6.4%), ν_{max} (KBr) 3100 (=CH), 1760 (CO) cm^{-1}; τ ($CDCl_3$) 2.35 (1H, s, H-3), 2.52 (5H, br s, Ph), 3.71 (1H, s, H-7) and 7.92 (3H, s, Me); mol. wt. found: 254.0531. $C_{15}H_{10}O_4$ calcd.: 254.0579. In addition to the molecular ion (P) which was also the base peak, the mass spectrum showed $P + 1$ (255.0605), $P—CO$ (226.0630, $C_{14}H_{10}O_3$ calcd.: 226.0630), $P—2(CO)$ (198.0665, $C_{13}H_{10}O_2$ calcd.: 198.0681) and $P—3(CO)$ (170.0747; $C_{12}H_{10}O$ calcd.: 170.0732) of relative intensities 20, 17, 28.5 and 26 respectively. This breakdown pattern is analogous to that observed for the other bifurandiones examined [e.g. III, IV and V (R = Me)].

Isomerisation of bifurandione III (R = Me)

No significant isomerisation was noted after heating this compound (0.4 g) in concentrated sulphuric acid (1.2 ml) at ≈80° for 5 h [conditions which isomerise [4] compound III (R = H)]. When a sample (0.52 g) was heated in the acid (1.5 ml) at 90-95° for 4½ h, the infrared spectrum of the recovered bifurandione (0.43 g) indicated partial, but not extensive, isomerisation to the *cis* form IV (R = Me) and further heating for 19 h at 95° allowed recovery of 0.30 g without significant change in spectrum.

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