Journal of Organometallic Chemistry, 141 (1977) 331–337

THERMAL AND PHOTOCHEMICAL OXYGENATION OF COBALTACYCLOPENTADIENE COMPLEXES WITH DIOXYGEN

FRIEDRICH-WILHELM GREVELS *
Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a.d. Ruhr (Germany)

YASUO WAKATSUKI * and HIROSHI YAMAZAKI
The Institute of Physical and Chemical Research, Wako-shi, Saitama 351 (Japan)

(Received May 27th, 1977)

Summary

(Cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadienes react with ground state dioxygen at 70°C and at room temperature with singlet dioxygen generated externally by microwave discharge to give 2-butene-1,4-diones. An intermediate cobalt complex of the dione has been isolated. The reaction can also be performed photochemically at room temperature.

Introduction

Oxidation of ligands in transition metal complexes by molecular oxygen has attracted much interest because of its importance as a model for industrial oxidation processes by transition metal catalysts [1]. Most of the reactions so far have been concerned with oxidation of simple ligands such as SO_2, CO, NO, N_3, phosphines, and H [2,3]. Although many organo-transition metal complexes are susceptible to dioxygen, few reports have appeared concerning the fate of larger organic ligands, e.g. dienes, in air-sensitive complexes. On the other hand, it is well known that organic conjugated dienes are typical singlet dioxygen acceptors to produce *endo*-peroxides; photosensitized reactions of dioxygen with dienes are widely investigated [4–7].

In this context we are investigating the reactivity of transition metal containing unsaturated substrates towards oxygen, especially with regard to the oxygenation of the organic moiety. In this paper we report the thermal and photochemical reactions of cobaltacyclopentadiene complexes with dioxygen.

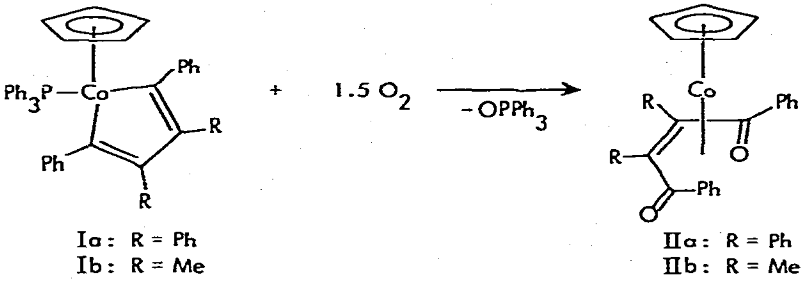
---

* Alexander von Humboldt fellow 1975–1977 at the Institut für Strahlenchemie, Mülheim a.d. Ruhr.

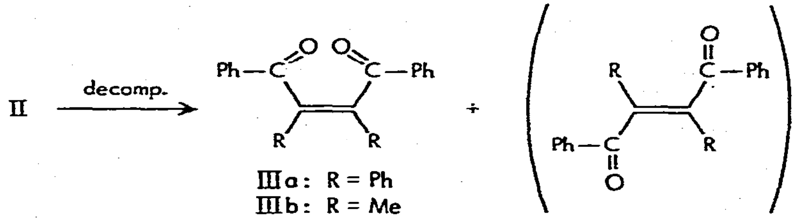
Results and discussion

Thermal reactions

At room temperature, (cyclopentadienyl)(triphenylphosphine)tetraphenylcobaltacyclopentadiene (Ia) and its dimethyldiphenyl analogue (Ib) are air-stable. However, they reacted smoothly when warmed. Thus, the brown benzene solution of Ia turned dark when heated to 70°C under dioxygen. Column chromatography of the mixture gave black crystals of composition $(C_5H_5)Co[(C_6H_5)_4C_4O_2]$ (IIa) and *cis*-dibenzoylstilbene (IIIa) in moderate yields. Prolonged heating yielded exclusively dibenzoylstilbene (>96% *cis*-isomer). Complex Ib reacted similarly to give IIb and *cis*-dibenzoyl-2-butene (IIIb).



(1)

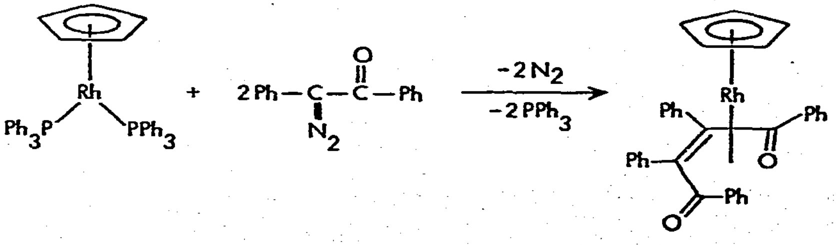


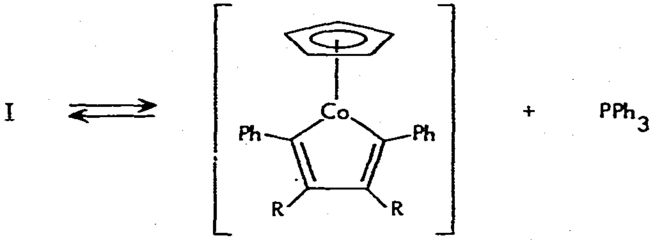
(2)

The structure of II as depicted in eq. 1 is in accord with the spectral data. Strong IR bands at 1635 cm^{-1} (IIa) and 1630 cm^{-1} (IIb) are assigned to ν(C=O) of an uncoordinated ketone group (IIIa and IIIb exhibit analogous but more intensive bands at the same positions), leaving the C=C double bond and the other ketone group to be coordinated to the metal. The ligand can be assumed to have retained the *cis*-configuration upon displacement from the metal. In the ^{1}H NMR spectra the cyclopentadienyl protons appear as sharp singlets at δ 4.85 (IIa) and 4.87 ppm (IIb), respectively, indicating that only one isomer is present. The spectrum of IIb exhibits two singlet methyl absorptions (δ 1.58 and 2.58 ppm) in accord with the unsymmetrical structure *.

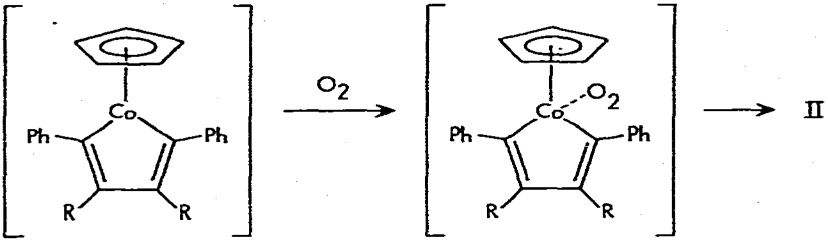
---

* The analogous rhodium complex formed by the reaction of cyclopentadienylbis(triphenylphosphine)rhodium with benzoylphenyldiazomethane shows an IR spectrum quite similar to that of IIa [8].





(3)



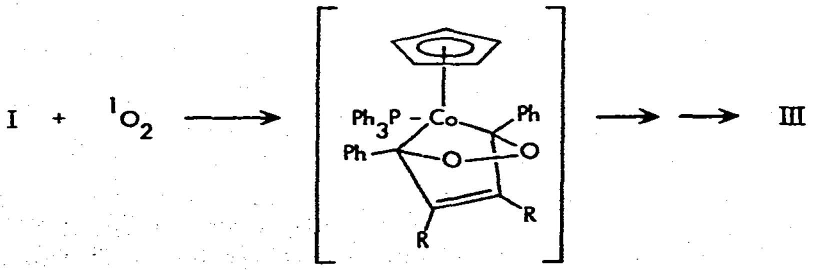
(4)

$$PPh_3 + 1/2\ O_2 \xrightarrow[(?)]{\text{metal-catalysed}} OPPh_3 \qquad (5)$$

The triphenylphosphine ligand in I can be replaced by another phosphine at 70°C but not at room temperature [9]; the dependence of reactivity on temperature is parallel to that with dioxygen. We suppose, therefore, that the first step (eq. 3) of the oxygenation reaction is thermal cleavage of the cobalt—phosphine bond, providing a free coordination site, to accomodate the oxygen molecule (step 4). The subsequent reaction of dioxygen with the diene moiety would take place within the coordination sphere of the metal.

Reaction with externally generated singlet dioxygen

Complex Ia reacted at room temperature with singlet dioxygen generated by microwave discharge to give IIIa in 41% yield. No dione complex could be isolated probably because of the small scale of the reaction. Since it is well established that singlet dioxygen behaves as a good dienophile with organic *cis*-1,3-dienes [4—7], a similar reaction scheme can be suggested:



(6)

Photochemical reactions

Irradiation of a benzene solution of I (high pressure mercury lamp, cut-off filter, $\lambda \geqslant 370$ nm) under dioxygen gave complexes II and *cis*- and *trans*-diones (IIIa: *cis* 73%, *trans* 27%; IIIb: *cis* 83%, *trans* 17%), together with phosphine oxide. Longer irradiation, as expected, increased the yield of III and decreased that of II. The ease of photochemical *cis* → *trans* isomerization of the free dione with $\lambda \geqslant 370$ nm was checked using authentic *cis*-dibenzoylstillbene. The relatively rich content of *trans*-isomer in III so obtained is thus attributed to *cis* → *trans* photoisomerization of originally *cis*-diones liberated from complex II.

The reaction may proceed either by phosphine—dioxygen exchange (eq. 3, 4) or by attack of singlet oxygen (eq. 6) produced by photosensitization. Complex I may act as a sensitizer in the latter case. Ruthenium(II) is known to produce singlet oxygen under irradiation [10] and doublet states of chromium(III) complexes are efficiently quenched by dioxygen [11]. However, since triphenylphosphine in Ia or Ib was replaced by ethyldiphenylphosphine in good yield by irradiation with the same wavelength ($\lambda \geqslant 370$ nm) as used in the photooxygenation reaction, it is also possible that the latter reaction occurs via phosphine—dioxygen exchange. Experiments to differentiate between the two alternatives have not yet resolved the mechanistic problem.

β-Carotene, a uniquely effective quencher for singlet molecular oxygen [5,12], totally quenched the photo-oxygenation reaction, whereas it did not affect the phosphine exchange reaction. It therefore seems likely that the photo-oxygenation reaction path involves participation of singlet molecular oxygen, although preliminary attempts to monitor the production of singlet oxygen directly were unsuccessful. As a further preliminary result, the carbomethoxy substituted complex Ic ($R = CO_2CH_3$) was found to decompose very slowly under irradiation in the presence of dioxygen but with no formation of ketone IIIc or its complex IIc. The same result was obtained when Ic was treated with microwave generated singlet dioxygen. This may be due to deactivation of the diene system towards singlet oxygen by the ester groups [13].

Experimental

Melting points are uncorrected and were determined on a Reichert hot stage melting point apparatus. Spectra were recorded using the following spectrometers: ^{1}H NMR, Bruker WH 270 and Varian A60 A; IR, Perkin—Elmer 621; UV, Brückl HRS 4001 C; Mass spectra, MAT CH5. Elemental analyses were performed by Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim (Ruhr).

Cobaltacyclopentadiene complexes Ia and Ib were prepared by the reaction of (cyclopentadienyl)bis(triphenylphosphine)cobalt with diphenylactylene or phenylpropyne as described before [15].

The *cis/trans* ratio of IIIa was determined by GLC (Packard 427, column OV 225, 10 m, 210°C, carrier gas H_2). The *cis/trans* ratio of IIIb was determined from ^{1}H NMR spectra.

Thermal oxygenation of I. In a 250 ml flask fitted with a reflux condenser were placed Ia (200 mg, 0.27 mmol) and benzene (80 ml). A slow stream of dioxygen was bubbled through the solution for 5 min to saturate the system with oxygen. The outlet of the condenser was then stoppered and the flask heated to 70°C for 8 h. Concentration of the dark reaction mixture and work-up by column chromatography on silicagel (Merck Kieselgel 60, column 2.5 cm in diameter, 7 cm long) yielded the following eluates, which were crystallized from n-hexane: (cyclopentadienyl)(tetraphenylcyclobutadiene)cobalt (yellow, eluted with 1/1 mixture of benzene/hexane, yield 5%); recovered Ia (brown, eluted with 1/1 mixture of benzene/hexane, yield 9%); IIIa (colourless, eluted with dichloromethane, yield 43 mg, 41%); IIa (dark-brown, eluted with dichloromethane, yield 47 mg, 34%); triphenylphosphine oxide (colourless, eluted with 10/1 mixture of dichloromethane/acetone, yield 74%). Black crystals of complex IIa begin to decompose above 150°C forming colourless needles of IIIa. IIa analysis: found: C, 77.45; H, 4.90; Co, 11.38. $C_{33}H_{25}O_2Co$ calcd.: C, 77.34; H, 4.92; Co 11.50%. ^{1}H NMR ($CDCl_3$): δ (ppm) 4.85 (singlet, C_5H_5), 6.7—8.0 (multiplet, C_6H_5). IR(KBr pellet): 3045, 1635, 1475, 1430, 1350, 1290, 1225, 1160, 1000, 835, 800, 750, 725 and 685 cm^{-1}. UV (CH_2Cl_2): 15.3×10^3 (ϵ = 260 l mol^{-1} cm^{-1}), 21.0 (sh, 1220), 25.0 (sh, 2580), 32.5 (sh, 14500), 40.1 (29100).

When the heating was continued for 24 h, (cyclopentadienyl(tetraphenylcyclobutadiene)cobalt (7%), IIIa (81 mg, 78%), and triphenylphosphine oxide (100%), were obtained.

Complex Ib (167 mg, 0.27 mmol) in benzene (80 ml) was treated similarly with dioxygen except that the heating was stopped after 2 h. Similar silicagel chromatography was used to yield the following: IIIb (colourless, eluted with 40/1 mixture of benzene/acetone, yield 17 mg, 24%); IIb (dark-brown, eluted with 40/1 mixture of benzene/acetone, yield 11 mg, 10%); triphenylphosphine oxide (colourless, eluted with 2/1 mixture of benzene/acetone, yield 97%). Dark-brown crystals of complex IIb melt with decomposition at 128—129°C. IIb analysis: found: C, 71.22; H, 5.44; Co, 15.21;, mol. wt. 388 (mass spectrum). $C_{23}H_{21}O_2Co$ calcd.: C, 71.13; H, 5.45; Co, 15.18%; mol. wt. 388.4. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.58 (singlet, CH_3), 2.58 (singlet, CH_3), 4.87 (singlet, C_5H_5), 7.3—7.8 (multiplet, C_6H_5). IR (KBr pellet): 3050, 2970, 1630, 1435, 1360, 1315, 1235, 1165, 960, 800, 780, 760, 700, 687 and 655 cm^{-1}. UV (CH_2Cl_2): 15.9×10^3 cm^{-1} (ϵ 198 l mol^{-1} cm^{-1}), 20.9 (1300), 25.5 (1640), 34.5 (16100), 41.2 (25400).

Reaction of Ia with singlet oxygen. A singlet oxygen generator Microton 200 of Electro-Medical-Supplies Co. was used. The geometry of the apparatus was essentially similar to that used by J.L. Dumas and B. Garnier [16]. Complex Ia (48 mg, 0.05 mmol) in dichlorobenzene (2.3 ml) was exposed to a stream of dioxygen for 3 h. Chromatographic work-up gave IIIa in 41% yield.

Photochemical oxygenation. A solution of Ia (300 mg, 0.4 mmol) in benzene (135 ml) was irradiated (Philips HPK 125 W high pressure mercury lamp, cut-off filter GWV, Glaswerk Wertheim, $\lambda \geqslant 370$ nm) under oxygen at 15°C. After 8 h the dark-brown mixture was concentrated and chromatographed as described in thermal oxygenation experiment to give recovered Ia (11%), IIIa (38 mg, 24%), complex IIa (90 mg, 44%), and triphenylphosphine oxide (85%). When the photoreaction was continued for 18 h, it gave IIIa (83 mg, 54%), IIa (79 mg, 88%), and phosphine oxide.

Similar irradiation of Ib (287 mg, 0.46 mmol) in benzene (135 ml) for 2 h followed by chromatographic work-up gave IIb (155 mg, 86%) and triphenylphosphine oxide; no IIIb was obtained. When irradiated for 9 h, the reaction gave IIIb (92 mg, 75%) and IIb (34 mg, 19%).

Photochemical phosphine exchange. A mixture of Ia (300 mg, 0.4 mmol) and ethyldiphenylphosphine (1 ml) in C_6H_6 (135 ml) was irradiated under argon, conditions as described for the photochemical oxygenation. After 26 h the mixture was chromatographed on silicagel (Merck Kieselgel 60, column 2.5 cm in diameter, 14 cm long). A brown band was eluted with 1/1 mixture of benzene/hexane. Concentration, and addition of hexane to the eluate gave brown crystals of (cyclopentadienyl)(ethyldiphenylphosphine)tetraphenylcobaltacyclopentadiene (yield 191 mg, 69%), m.p. 124—127°C (dec.) (Found: C, 81.10; H 5.95; Co, 8.51. $C_{47}H_{40}PCo$ calcd.: C, 81.26; H, 5.80; Co 8.48%). ^1H NMR (C_6D_6): δ (ppm) 0.7 (quintet, J(H,H) 7.5, J(H,P) 15 Hz, CH_3), 2.38 (quintet, J(H,P) 7.5 Hz, CH_2), 4.70 (singlet, C_5H_5), 6.7—7.4 (multiplet, C_6H_5). Similar reaction of Ib with ethyldiphenylphosphine, concentration of the resulting mixture, and addition of hexane gave black crystals of (cyclopentadienyl)(ethyldiphenylphosphine)-3,4-dimethyl-2,5-diphenylcobaltacyclopentadiene (yield 214 mg, 81%), which was further recrystallized from benzene/hexane, m.p. 160—162°C (dec.) (Found: C, 77.91; H, 6.31; Co, 10.41. $C_{37}H_{36}PCo$ calcd.: C, 77.87; H, 6.36; Co, 10.33%). ^1H NMR (C_6D_6): δ (ppm) 0.68 (quintet, J(H,H) 7.5, J(H,P) 15 Hz, CH_3 in ethyl group), 1.76 (doublet, J(P,H) 1.8 Hz, CH_3 at cobalta-ring), 2.24 (quintet, J(P,H) 7.5 Hz, CH_2), 4.53 (singlet, C_5H_5), 6.8—7.6 (multiplet, C_6H_5).

Effect of β-carotene on photoreaction of Ia. A solution of Ia (297 mg, 0.4 mmol) in benzene (92 ml) was irradiated (Philips HPK 125 W high pressure mercury lamp, cut-off filter FW 161, Glaswerk Wertheim, $\lambda \geqslant 500$ nm) under oxygen at 15°C for 6 h. Column chromatography similar to that described for the thermal oxygenation yielded Ia (55%), IIIa (7 mg, 5%), and IIa (47 mg, 23%). When this reaction was carried out in the presence of β-carotene (0.004 mmol), only recovered Ia (76%) was obtained, and no measurable amount of IIa nor IIIa.

A solution of Ia (200 mg, 0.27 mmol) and ethyldiphenylphosphine (0.7 ml) in benzene (80 ml) was irradiated in a similar apparatus for 24 h. Addition of a large amount of hexane to the concentrated reaction mixture gave brown crystals which were washed with hexane several times (yield 190 mg). The ^1H NMR spectrum showed that 10% of complex Ia had exchanged phosphine. The same result was obtained when the reaction was carried out in the presence of β-carotene (0.0027 mmol).

Acknowledgements

We are indebted to the Alexander von Humboldt-Stiftung for supporting this work by a research fellowship to Y.W. during his stay at the Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung (Mülheim a.d. Ruhr). We thank our colleagues Dr. H. Henneberg (mass spectra), W. Riemer (NMR, UV, and IR spectra), Dr. G. Schomburg (gas chromatography), and their coworkers for their help. Collaboration and helpful discussions with Dr. H.J. Kuhn are gratefully acknowledged.

References

1 C.R. Adams, Ind. Eng. Chem., 61 (1969) 30.
2 J.S. Valentine, Chem. Rev., 73 (1973) 235.
3 G. Henrici-Olivé and S. Olivé, Angew. Chem., 86 (1974) 1.
4 K. Gollnick, Advan. Photochem., 6 (1968) 1.
5 D.R. Kearns, Chem. Rev., 71 (1971) 395.
6 W. Adam, Chem.-Ztg., 99 (1975) 142.
7 G. Ohloff, Pure Appl. Chem., 43 (1975) 481.
8 P. Hong and H. Yamazaki, unpublished results.
9 H. Yamazaki, unpublished results.
10 J.N. Dames, D. Diemente and E.W. Harris, J. Amer. Chem. Soc., 95 (1973) 6864.
11 A. Pfeil, J. Amer. Chem. Soc., 93 (1971) 5395.
12 C.S. Foote and R.W. Denny, J. Amer. Chem. Soc., 90 (1968) 6233.
13 G.O. Schenck, Angew. Chem., 64 (1952) 12.
14 H.J. Kuhn, R. Straatmann and D. Schulte-Frohlinde, J. Chem. Soc. Chem. Commun., (1976) 824.
15 Y. Wakatsuki, P. Kuramits and H. Yamazaki, Tetrahedron Lett., (1974) 4549.
16 J.L. Dumas and B. Garnier, J. Chim. Phys. Physicochim. Biol., 72 (1975) 1045.