18. Rhodium-Catalyzed C, C-Double Bond Cleavage by Molecular Oxygen

by Helmut Bönnemann[1]), Washington Nunez[2]) and Dieter M.M. Rohe[3])

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim-Ruhr

Summary

Acetylacetonatorhodiumolefin systems, allylrhodium complexes, or $(Ph_3P)_3RhCl$ catalyzed the conversion of alkenes and molecular oxygen to carbonyl compounds *via* C=C-bond cleavage. For example, 2,3-dimethyl-2-butene was transformed into acetone. Butadiene and isoprene also undergo oxidative C=C-bond cleavage to form acrylaldehyde and related compounds.

Since the isolation of dioxygen complexes of the type $(Ph_3P)_2MO_2$ (M = Ni, Pd, Pt) by *Wilke et al.* [1] in 1967 and the discovery that they are active for the catalytic oxidation of triphenylphosphine, several attempts have been made to develop a homogeneous olefin-oxidation process using group VIII metal complexes. Initially *Dudley, Read & Walker* [2] reported that the co-oxygenation of 1-alkenes and triphenylphosphine by molecular oxygen is catalyzed by a dimeric O_2-complex derived from $(Ph_3P)_3RhCl$ [3] [6] and gives mainly methyl ketones besides equimolar amounts of triphenylphosphine oxide *(Scheme 1)*. Later, *Mimoun* [4] used $RhCl_3 \cdot 3 H_2O : Cu(ClO_4)$ as the catalyst for the ketonization of alkenes according to *Scheme 1*.

Scheme 1

$$R-CH=CH_2 + PPh_3 + O_2 \xrightarrow{(Ph_3P)_3RhX} R-\overset{O}{\overset{\|}{C}}-CH_3 + Ph_3P=O$$
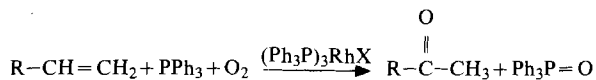
L = PPh₃; X = Cl, CN, OCN, SCN

During our investigations of Rh-catalyzed alkene-reactions [5] we explored the catalytic oxygenation of some olefinic substrates by molecular oxygen. If air bubbled through a toluene/styrene (1) solution of acetylacetonatorhodium at 80° the only reaction observed is the conventional formation of acetophenone (2) *(Scheme 2)*.

Scheme 2

$$Ph-CH=CH_2+\tfrac{1}{2}O_2 \xrightarrow[80°]{} Ph-C-CH_3$$

1   2
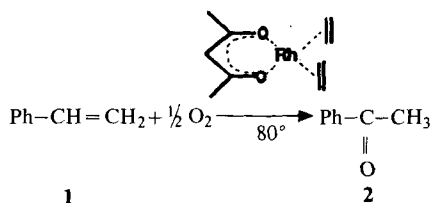
However, by carrying out the same reaction in an autoclave charged with dry compressed air at 80° and 50 bar, the oxidative cleavage of the alkene double bond *(Scheme 3)* becomes the predominant pathway of the Rh-catalyzed reaction[4]).
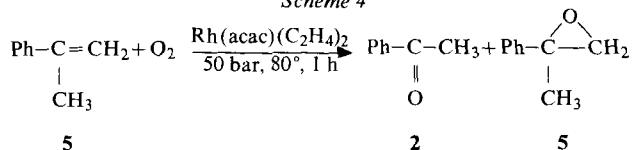
Scheme 3

$$Ph-CH=CH_2+O_2 \xrightarrow[80°]{50\ bar,\ air,} Ph-CH+[O=CH_2]$$

1   3

$$HO-CH_2O-[CH_2O]_n-CH_2OH$$

4
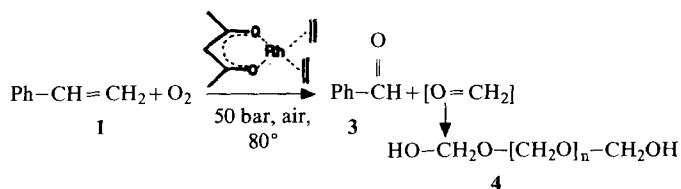
Under these conditions in 1 h, 26% of alkene loaded were converted, yielding 55 mol of benzaldehyde (3) per mol of catalyst; 2 was found only in traces. No benzoic acid was detected. At higher alkene conversions (50–60%) and with 4–5 h reaction time greater amounts of polymeric styrene and the by-product 2 were formed. Formaldehyde – the second product of catalytic C=C-bond cleavage – was identified in the form of moderate amounts of polyoxymethylene (4) *(Scheme 3)*.

The analogous reaction with α-methylstyrene (5) gave 1 as well as traces of the oxirane 5 *(Scheme 4)*.

Scheme 4

$$Ph-C=CH_2+O_2 \xrightarrow[50\ bar,\ 80°,\ 1\ h]{Rh(acac)(C_2H_4)_2} Ph-C-CH_3+Ph-C-CH_2$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad ||\qquad\quad |$$
$$CH_3\qquad\qquad\qquad\qquad\qquad\qquad O\qquad CH_3$$

5   2   5

Even more surprisingly, the catalytic oxidation of 2,3-dimethyl-2-butene (6) yielded predominantly acetone (7) as a result of the fission of the tetrasubstituted double bond. The oxirane 8 was a side-product of the Rh-catalyzed reaction and the ratio depended on the alkene conversion. The C_6-alcohol 9 and the ketone 10 were found only in small amounts *(Scheme 5)*.

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[4]) Recently *Carlton & Read* have reported the formation of 3 as a by-product in the formation of 2 using *Wilkinson's* catalyst (RhCl(PPh₃)₃) in the normal pressure O_2-oxidation of styrene [6].

Scheme 5
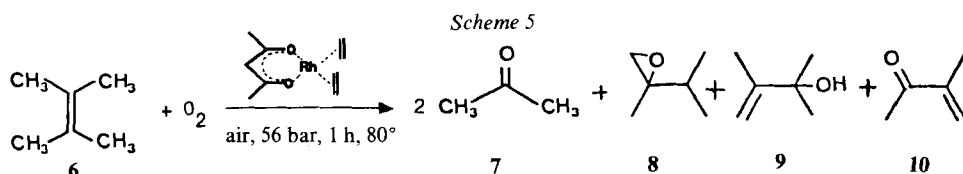
The proportion of the products as well as the turnover number strongly depended on the nature of the Rh-complex catalyst *(Table 1)*. Acetylacetonato-substituted Rh-alkene compounds in general appear to be the most selective systems for the oxidative C=C-bond cleavage *(Scheme 5);* cyclopentadienyl- and allyl-Rh-complexes as well as *Wilkinson's* catalyst are also effective. In contrast, the dimeric chlororhodium-alkene systems show almost no catalytic activity. It appears by comparison that Rh-complexes containing good leaving groups such as ethylene are more reactive than the corresponding cyclooctadiene or carbonyl complexes which are more stable.

Table 1. *Oxidation of 2,3-dimethyl-2-butene (6) at 80° with air at 50 bar using Rh-catalysts[a])*

| Catalyst	Alkene 6			Turnover-number mol product/Rh/h				Yield[b]) (%)			
	mmol	Conv. %	Cat. mmol	7	8	9	10	7	8	9	10
Rh(acac)(C₂H₄)₂	42.9	75.5	0.19	47.9	34.3	9.9	3.3	28.1	20.1	5.8	1.9
Rh(acac)(C₃H₅)₂	40.5	75.8	0.21	38.5	5.4	21.9	–	26.4	3.7	15.0	–
Rh(F₆acac)(C₂H₄)₂	51.2	21.7	0.20	20.1	0.8	–	–	36.3	1.0	~	–
Rh(acac)DVCB	51.7	26.5	0.21	17.1	–	–	–	26.3	~	~	–
Rh(acac)COD	39.4	62.2	0.45	6.8	1.0	5.1	1.0	17.7	1.9	9.4	1.0
Rh(F₆acac)COD	42.8	11.0	0.26	3.0	~	–	–	16.7	~	~	–
Rh(acac)(CO)₂	39.4	6.9	0.79	–	–	–	no reaction				
[ClRh(C₃H₅)₂]₂	40.5	58.9	0.10	44.0	–	31.0	3.2	18.8	–	13.1	1.4
Rh(Cp)(DVCH)	38.0	60.8	0.25	24.6	4.4	4.0	1.0	26.6	*4.8*	4.3	1.4
Rh(Cp)(COD)	37.0	61.1	0.65	10.0	1.0	6.9	1.0	28.6	2.8	*19.9*	1.6
Rh(C₃H₅)₃	39.4	52.5	0.09	39.0	4.2	22.2	2.8	16.9	1.8	9.7	1.2
[RhCl(C₂H₄)₂]₂	39.4	33.2	0.24	1.0	1.0	1.5	–	1.0	2.0	2.7	–
[RhCl(CO)₂]₂	39.4	2.5	0.15	–	~	–	–	no reaction			
RhCl(PPh₃)₃	40.5	60.1	0.11	29.7	1.0	*32.4*	3.2	16.9	0.5	14.4	1.3

[a]) Abbreviations: acac = acetylacetonato; Cp = cyclopentadienyl; COD = 1,5-cyclooctadiene; DVCB = *cis*-1,2-divinylcyclobutane; DVCH = *trans*-1,2-divinylcyclohexane; F₆acac = bis(trifluoromethylacetylacetonato).

[b]) Based on reacted substrate; results corrected for non-Rh-catalyzed products.

In contrast to the findings of *Furhop et al.,* using Co-catalysts [7] the Rh-catalyzed reaction of 2-methyl-2-pentene (11) with compressed air also resulted in C=C-bond cleavage, whereby the isopropylidene group, is cleared in the form of acetone (7). The other part of the 11 might be expected to be transformed to propanal (12) which, however, was found only in traces. Furthermore a considerable amount of unidentified residue was obtained. In a side reaction the conventional C₆ oxidation products 13–15 shown in *Scheme 6* were formed.

Scheme 6

| 11 | | 7 | 12 | 13 | 14 | 15 |
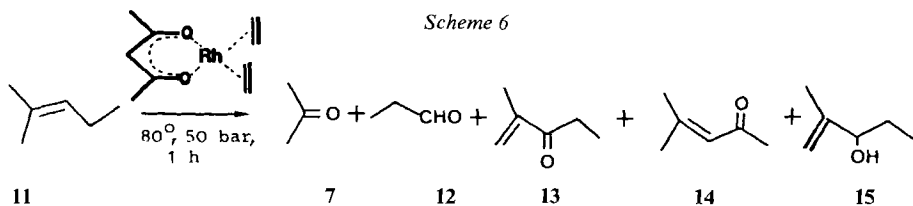
The cleavage of the terminal isopropylidene group in the form of acetone by Rh-catalyzed oxidation with air under pressure appears to be general. For example myrcene (**16**) gave some acetone (**7**) beside a large part of unidentified residues (*Scheme 7*).
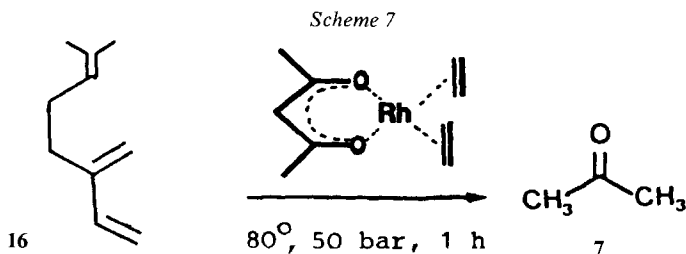
Scheme 7

Methylidenecyclopentane (**17**) reacted with air under pressure to give cyclopentanone (**18**) in presence of the Rh-catalyst; formaldehyde or related products could not be detected (*Scheme 8*). 1,3-Butadiene (**19**) reacted with O_2 in toluene in the presence of the Rh-complex to give acrylaldehyde (**20**) which, under the reaction conditions, was partly transformed to the *Diels-Alder* adduct **21**. The second C=C-bond in 1,3-dienes appeared to be unreactive against oxidative cleavage and no trace of glyoxal could be detected (*Scheme 9*).
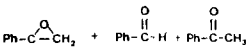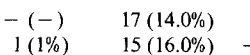
Scheme 8

Scheme 9
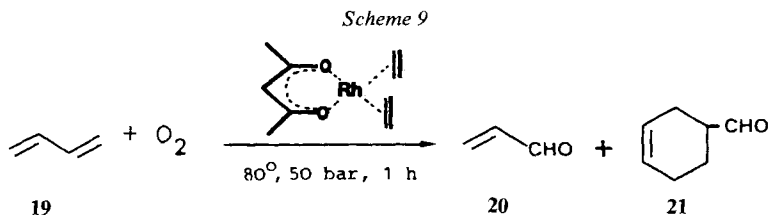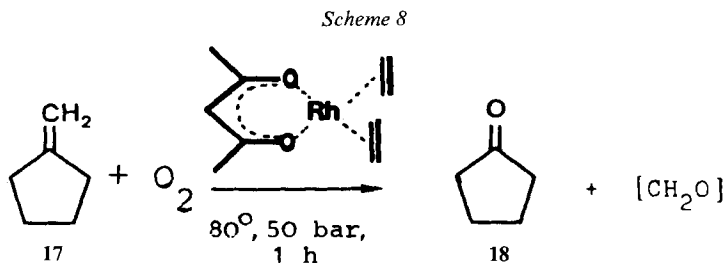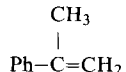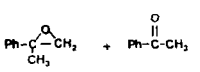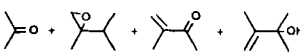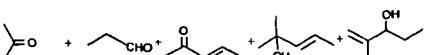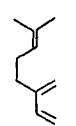
Table 2. *Rh-catalyzed oxidative C=C-bond cleavage of some alkenes at 75–80° with air at* ca. *50 bar*

Catalyst	Alkene (conversion %)	Products Activity[a]) (yield)[b])

	PhCH=CH$_2$	Ph-C(O)-CH$_3$ + Ph-C(O)-H + Ph-C(O)-CH$_3$
Rh(acac)(C$_2$H$_4$)$_2$	(57.3%)	– (–) 17 (14.0%) 5 (4.1%)
RhCl(PPh$_3$)$_3$	(21.6%)	1 (1%) 15 (16.0%) – (–)

	CH$_3$ | Ph-C=CH$_2$	Ph-C(O)-CH$_2$CH$_3$ + Ph-C(O)-CH$_3$
Rh(acac)(C$_2$H$_4$)$_2$	(30.9%)	27 (12.3%) 100 (41.1%)

Rh(acac)(C$_2$H$_4$)$_2$	(75.6%)	47.9 (28.1%) 34.3 (20.1%) 3.3 (1.9%) 9.9 (5.8%)
RhCl(PPh$_3$)$_3$	(60.1%)	29.7 (16.9%) 1 (0.5%) – (–) 3.2 (1.3%)

Rh(acac)(C$_2$H$_4$)$_2$	(75.7%)	29.8 (6.0%) – (–) 2.0 (< 1%) 10.0 (2.0%) 5.0 (1.0%)
RhCl(PPh$_3$)$_3$	(68.0%)	18.7 (6.8%) 1.0 (< 1%) 1.0 (< 1%) 6.5 (2.5%) 2.0 (< 1%)

Rh(acac)(C$_2$H$_4$)$_2$	(93.0%)	16.5 (2.3%) 42.0 (2.0%)

|	CH$_2$	
Rh(acac)(C$_2$H$_4$)$_2$	(60.0%)	12.2 (2.0%)
RhCl(PPh$_3$)$_3$	(56.1%)	65.0 (4.0%)

		CH$_2$=CHCHO + -CHO
Rh(acac)(C$_2$H$_4$)$_2$	(94.7%)	27.3 (1.0%) 7.3 (0.3%)

		CH$_2$=C(CH$_3$)-CHO +
Rh(acac)(C$_2$H$_4$)$_2$	(59.0%)	9.7 (1.0%) 12.6 (1.3%)

Rh(acac)(C$_2$H$_4$)$_2$ RhCl(PPh$_3$)$_3$		No reaction

a) $\dfrac{\text{Mol-product}}{\text{Mol-catalyst} \cdot \text{h}}$

b) Based on converted alkene.

Scheme 10

22   + O$_2$ → (80 °, 50 bar, 1 h)   23 (CHO)   +   24
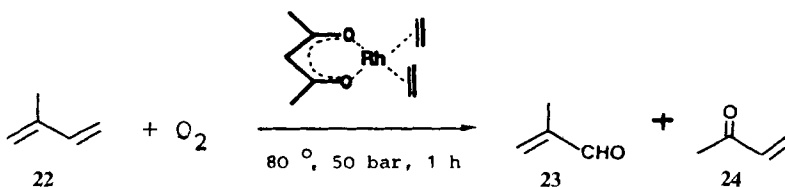
In the case of isoprene (**22**), almost equimolar amounts of methacrylaldehyde (**23**) and methylvinylketone (**24**) were formed *(Scheme 10)* indicating that the CH$_3$-substituent exerts no directing influence on the C=C-bond cleavage.

The results with different alkenes are summarized in *Table 2*.

The Rh-catalyzed C=C-bond cleavage can formally be regarded as a double decomposition by singlet oxygen *(Scheme 11)* analogous to a proposal by *Kim et al.* [8] for the formation of formaldehyde from ethylene and oxygen on heterogeneous catalysts.

Scheme 11

Scheme 12

R = CH$_3$
X = acac
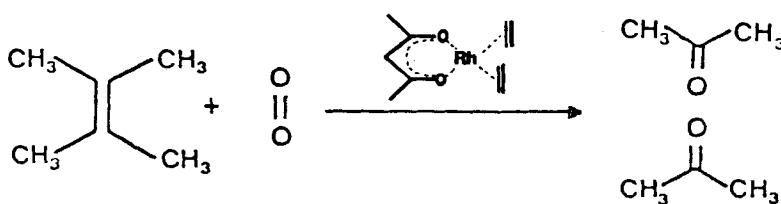
A plausible mechanism involving the stepwise formation of the 1,2-dioxa-3-rhodacyclopentane **25** is shown above *(Scheme 12)*. *Sheldon & van Doorn* [9] have demonstrated that a Pd-analogue to **25** undergoes stochiometric decompositions to give the corresponding ketone.

Catalyzed oxidative cleavage of alkenes by molecular oxygen is relatively unexplored and work is in progress to clarify the merits of the reaction [10].

Experimental Part
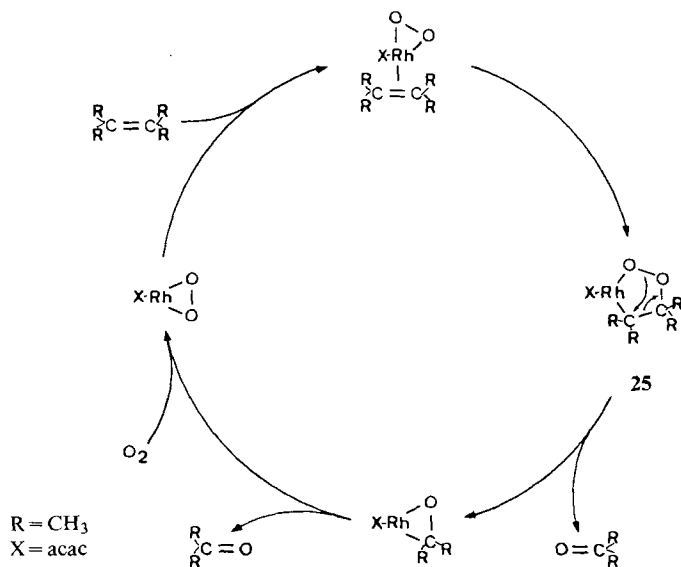
1. *Preparation of the new complexes.* The new complexes Rh(acac)(DVCB), Rh(F$_6$acac)(C$_2$H$_4$)$_2$ and Rh(Cp)(DVCH) were prepared in a manner analogous to that reported by *Cramer* [11] from the reactions of RhCl$_3 \cdot$ 3 H$_2$O with the appropriate alkenes and subsequent replacement of the Cl-ligand by anions.

The results summarized in *Table 1* were obtained under standard conditions (50 bar compressed air, 80°, reaction time 1 h). The amount of identified oxidation products in the mixtures was adjusted by deducting the amount formed in an identical reaction carried out without catalyst. Typical experiments are described below.

2. *Air oxidation of 2,3-dimethyl-2-butene* (**6**) *with Rh(acac)(C$_2$H$_4$)$_2$*. A mixture of 50.1 mg (0.19 mmol) of Rh(acac)(C$_2$H$_4$)$_2$ [11] in 8.6 g toluene and 3.6 g (42.86 mmol) of **6** was placed in an evacuated 200 ml stainless steel autoclave with magnetic stirring (loss *ca.* 0.2 g). The autoclave was filled with 9 l dry air (19.6 mol% O$_2$) at r.t. and 50 bar. The mixture was stirred vigorously at 80±1° for 1 h (max. pressure 56 bar) and the autoclave cooled to 10° then vented carefully and 8.6 l gas containing 12.6 mol-% O$_2$ was measured with a gasometer and analyzed by MS. The consumption of O$_2$ was 0.8 g. The crude product (12.0 g), a yellow-brown liquid, was transferred to a 250 ml 2-necked flask, leaving 0.2 g of a yellow residue in the autoclave. *Ca.* 1 g of FeSO$_4$ was added and the liquid was condensed at 20–50° and 10^{-4} mbar. Distillate colorless: 11.6 g; (residue in the flask: 0.4 g).

Table 3. *GC.* (50-m column *Carbowax 20 M/1019 C*) *of* **6**

Product	Area (%)	Factor	Mass (g)	mmol
2,3-Dimethyl-2-butene (**6**)	7.42	1.10	0.878	10.45
Acetone (**7**)	5.03	1.95	1.056	18.20
2-Methyl-2-isopropyloxirane (**8**)	4.42	1.37	0.651	6.51
3-Methyl-3-buten-2-ol (**9**)	1.23	1.42	0.188	1.88
3-Methyl-3-buten-2-one (**10**)	0.32	1.50	0.052	0.62
Toluene	77.10	1.00	8.296	–
Not identified	4.47	1.00	0.481	(4.81

Yield: see *Table 2*.

Catalytic turnover number: 47.9 mol **6** per mol catalyst transformed into acetone (**7**); 34.3 mol 2,3-dimethyl-2-butene per mol catalyst transformed into oxirane **8**.

3. *Air oxidation of styrene* (**1**) *with Rh(acac)(C$_2$H$_4$)$_2$*. A mixture of 95 mg (0.37 mmol) of Rh(acac)(C$_2$H$_4$)$_2$ [11] in 4.5 g toluene and 40.8 g (392 mmol) of **1** was placed in an evacuated 200 ml stainless steel autoclave with magnetic stirring (loss 0.2 g). The autoclave was filled with 6.4 l dry air (19.6 mol-% O$_2$) at r.t. and 45 bar. The mixture was stirred vigorously at 75±1° for 5 h (max. pressure 49 bar) and the autoclave cooled to 10° then vented carefully and 5.2 l gas containing 0.6 mol-% O$_2$ was measured with a gasometer and analyzed by MS. The consumption of O$_2$ was 1.64 g. The crude product (44.9 g), a red viscous liquid, was transferred to a 500 ml 2-necked flask, leaving in the autoclave 0.8 g of a high-

viscous liquid and 0.4 g of a white residue (polyoxymethylene identified by IR. and MS.). The crude product was condensed in 2 steps, first at 20° and 10^{-4} mbar (distillate 1: 22.4 g) and then at 100° and 10^{-4} mbar (distillate 2: 2.9 g). The residue amounted to 18.4 g.

The distillation residue was dissolved in ether and 14.2 g polystyrene (IR.) was precipitated with EtOH, leaving 4.2 g of a viscous liquid. Yield: see *Table 2*.

Catalytic turnover number: 84.9 mol 1 per mol catalyst transformed into benzaldehyde (**3**); 25 mol 1 per mol catalyst transformed into acetophenone (**2**); (35.9 mol 1 per mol catalyst transformed into formaldehyde.).

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