

## RHODIUM-CATALYZED C–C COUPLING OF 1,3-DIENES WITH 3-ALKENOIC ACIDS

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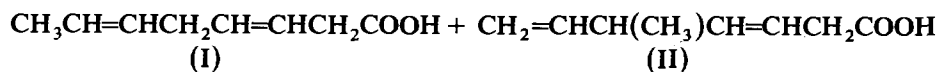
### Summary

The rhodium-catalyzed reaction of 1,3-dienes with 3-alkenoic acids leads to a class of 3,6-dienoic acids not readily accessible by other ways. Steric effects profoundly influence the course of the reaction, in respect of both the catalytic efficiency and the selectivity. A high proportion (93%) of linear product was obtained from the reaction of butadiene with 3-butenic acid in the presence of a cationic rhodium complex. Complete regioselectivity at the diene-unsaturated acid coupling site was observed for butadiene and 3-pentenoic acid. 4-Pentenoic acid gave the same product as 3-pentenoic acid.

Metallacyclic intermediates appear to be involved in these reactions.

### Introduction

We have previously briefly described a new synthesis, consisting of the reaction of 1,3-dienes with 3-butenic acid, according to eq. 1 (written for the simplest case) [1]:



The reaction is catalyzed by rhodium(I) complexes and characterized by a high degree of regioselectivity, compounds I and II being formed in a 85/15 ratio. Both products result from exclusive addition of a diene carbon to the terminal carbon atom of the butenoic chain. 3*E*,6*E* and 3*Z*,6*E* isomers were formed in comparable amounts. Another interesting aspect noted for this reaction was the unprecedented catalytic efficiency, which exceeded 20,000 cycles per mol of catalyst.

The present paper is concerned with the reactions of various dienes and butenoic acids in the presence of various rhodium complexes.

## Results

### Dienes

The following acids were obtained from the reaction of the listed dienes with 3-butenic acid:

butadiene	I,II [1]
isoprene:	$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{COOH}$ (III) [2]
1,3-pentadiene:	$\text{CH}_3\text{CH}=\text{CHCH}(\text{CH}_3)\text{CH}=\text{CHCH}_2\text{COOH}$ (IV) $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{COOH}$ (V)
2,4-hexadiene:	$\text{CH}_3\text{CH}=\text{CHCH}(\text{CH}_2\text{CH}_3)\text{CH}=\text{CHCH}_2\text{COOH}$ (VI) $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3)\text{CH}=\text{CHCH}_2\text{COOH}$ (VII)
1,3,7-octatriene	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{COOH}$ (VIII)

3*Z*,6*E* and 3*E*,6*E* isomers were found to be present.

Table 1 gives details of yields and catalytic efficiencies.

Some by-products are formed by further reaction of butadiene with the 3,6-dienoic acids produced in the main reaction. Thus 4,4-di(3-butenyl)-3-butenic acid,  $(\text{CH}_3\text{CH}=\text{CHCH}_2)_2\text{C}=\text{CHCH}_2\text{COOH}$  (IX), is formed as by-product of the reaction of butadiene with 3-butenic acid. Cyclopentadiene gave only the Diels-Alder adduct with 3-butenic acid.

### Butenoic acids

Table 2 presents results for reactions of various 3-butenic acids with 1,3-butadiene. The following acids were obtained:

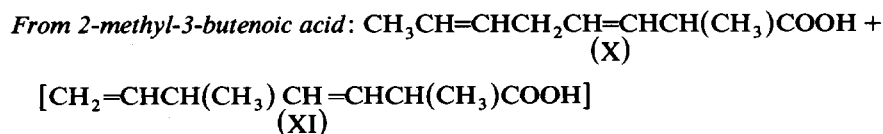


TABLE 1

REACTIONS OF DIENES WITH 3-BUTENOIC ACID;  $\text{RhCl}(\text{PPh}_3)_3$  AS CATALYST (120°C, 14 h)

Diene	Diene/metal molar ratio <sup>a</sup>	Butenoic acid/metal molar ratio <sup>a</sup>	Products <sup>b</sup> (Yield (%))	Product/catalyst molar ratio
Butadiene	35000	30000	I (67), II (7.5)	22400
Isoprene	4000	3000	III (56)	1680
1,3-Pentadiene	340	290	IV (67), V (22)	257
2,4-Hexadiene	150	100	VI (27), VII (28)	55
1,3,7-Octatriene	150	100	VIII (26), isomers <sup>c</sup> (38)	69

<sup>a</sup> The molar ratio of substrates to metal was varied according to the reactivity of system. <sup>b</sup> Yield based on butenoic acid initially taken, determined by GLC with internal standard; most of the butenoic acid was recovered unchanged along with small amounts of crotonic acid. <sup>c</sup> Not identified.

TABLE 2

REACTION OF BUTADIENE WITH VARIOUS 3-BUTENOIC ACIDS;  $\text{RhCl}(\text{PPh}_3)_3$  AS CATALYST (120°C, 14 h)

3-Butenoic acid	Diene/metal molar ratio <sup>a</sup>	Butenoic acid/metal molar ratio <sup>a</sup>	Product (Yield (%)) <sup>b</sup>	Mol product/mol catalyst
2-Methyl	290	165	X (68), XI (9)	126
3-Methyl	800	525	XII (64), XIII (15)	415
4-Methyl	150	130	XIV (73)	95
4,4-Dimethyl	300	100	XV (50)	50

<sup>a</sup> The diene/metal and butenoic acid/metal ratios were adjusted according to the reactivity of the system. <sup>b</sup> Based on the 3-butenoic acid initially taken. Most butenoic acids were recovered unchanged, except for 2-methylbutenoic acid, which was completely isomerized to 2-methyl-2-butenoic acid.

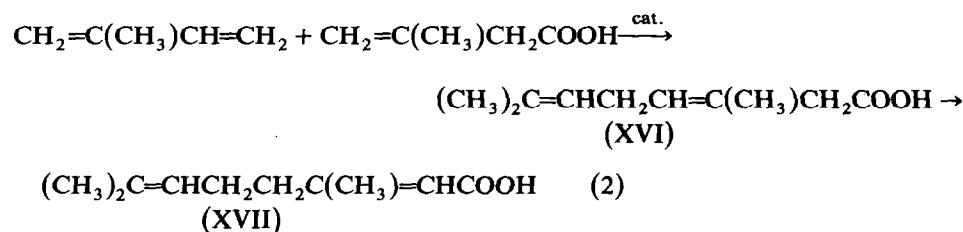
From 3-methyl-3-butenoic acid:  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{COOH} +$   
(XII)

$[\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{COOH}]$   
(XIII)

From 4-methyl-3-butenoic acid:  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{COOH}$   
(XIV)

From 4,4-dimethyl-3-butenoic acid:  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{C}(\text{CH}_3)_2\text{CH}=\text{CHCOOH}$   
(XV)

Reactions of butadiene homologues with 3-butenoic acid homologues gave poor results. Thus the reaction of isoprene with 3-methyl-3-butenoic acid (eq. 2), which was expected to give XVI, readily isomerizable to geranic acid (XVII) [3], gave a complex isomeric mixture. The latter was converted by catalytic hydrogenation on Pd/C into at least four compounds; one of the GLC peaks had a retention time corresponding with hydrogenated XVI, but in view of the complexity of the mixture and the low catalytic efficiency (ca. 20 mol total product per mol of catalyst), no further work was carried out on this system.



### Catalysts

The results of the use of different  $\text{Rh}^{\text{I}}$  complexes with and without an excess of ligand are reported in Table 3.

A comparison of the two sets of experiments performed with and without an excess of phosphine shows that the cationic rhodium complex is the most sensitive to the excess of this ligand which tends to cause levelling off of the ratio of linear to branched product (I/II).

TABLE 3

REACTION OF BUTADIENE AND 3-BUTENOIC ACID IN THE PRESENCE OF RHODIUM COMPLEXES (3500/30000/1 molar ratio) (at 120°C for 14 h)

Complex	Excess L/Rh complex = 0			Excess L/Rh complex = 32		
	Yield (%) <sup>a</sup>	Mol product/ Mol catalyst	I/II	Yield (%) <sup>a</sup>	Mol product/ Mol catalyst	I/II
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	74.8	22400	8.8	67.5	20200	8.3
RhH(PPh <sub>3</sub> ) <sub>4</sub>	47.1	14100	10.6	67.5	20200	7.6
Rh(CH <sub>3</sub> COO)(PPh <sub>3</sub> ) <sub>3</sub>	39.0	11600	9.1	56.0	16700	8.2
[Rh(COD)(PPh <sub>3</sub> ) <sub>3</sub> ]PF <sub>6</sub> <sup>b</sup>	15.0	4500	13.0	57.0	17100	7.7

<sup>a</sup> Yield of I+II based on butenoic acid taken. Most of this acid was recovered unchanged along with small amounts of crotonic acid. <sup>b</sup> COD = 1,5-cyclooctadiene.

TABLE 4

REACTION OF BUTADIENE WITH 3-BUTENOIC ACID IN THE PRESENCE OF 1/2 [RhCl(COT)<sub>2</sub>]<sub>2</sub> + 3L (L = LIGAND) (35000/30000/1 molar ratio) (at 120°C for 14 h)

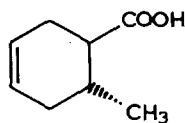
L	$\nu(\text{CO})$ (cm <sup>-1</sup> )	$\theta$ (°) <sup>a</sup>	Mol I + II/ Mol catalyst	Proportion of linear product (%)
P-i-Pr <sub>3</sub>	2059	160	3300	87
P-n-Bu <sub>3</sub>	2060	132	15000	88
PPh <sub>3</sub>	2069	145	22000	90
P(O-i-Pr) <sub>3</sub>	2076	130	800	72
P(O-n-Bu) <sub>3</sub>	2077	109	2000	76
P(OPh) <sub>3</sub>	2085	128	16500	89

<sup>a</sup> Ligand electronic and steric parameters [4].

Table 4 presents details of the catalytic efficiencies and the proportion of linear product for a series of rhodium complexes obtained in situ by adding different phosphorus compounds to [RhCl(COT)<sub>2</sub>]<sub>2</sub> (COT = cyclooctene) (3 mol of ligand per g atom of rhodium).

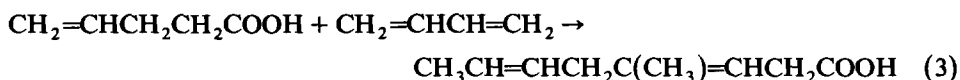
#### Other unsaturated acids

2 or 4-alkenoic acids did not react in the same way as 3-alkenoic acids. 2-Alkenoic acids gave the Diels–Alder adduct; for example crotonic acid gave methylcyclohexenylcarboxylic acid XVIII [5].



(XVIII)

4-Alkenoic acids reacted only after isomerization to 3-alkenoic acids. Thus 4-pentenoic acid gave the following reaction (eq. 3):



A blank experiment without butadiene showed isomerization to 3-pentenoic acid.

### *Catalyst inactivation*

Loss of activity of the rhodium catalyst was observed in the presence of 2-alkenoic acids (crotonic); and also in the presence of CO in the gas phase. A slow evolution of CO occurred during the reaction, and at the end of the reaction the catalyst was recovered mainly as  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ . This is still active if used in the absence of gaseous CO. The reaction did not proceed under a CO atmosphere.

### *Identification of products*

The mass spectra are in accord with the proposed structures. Hydrogenation on Pd/C gave the number of the double bonds. UV spectra did not show absorptions at wavelengths above  $220 \text{ m}\mu$ , thus all products turned out to contain double bonds which were not conjugated with each other. IR spectra ( $\text{cm}^{-1}$ ) of disubstituted double bonds were observed at 970–977s and 825–830w. The absence of conjugation of the double bonds was further confirmed by the  $^1\text{H}$  NMR spectra, which showed signals from double bond protons below  $\delta 6$ , except for compound XV, which has a double bond conjugated with the carboxylic group.

3*E* and 3*Z* isomers were found to be present for each 3-unsaturated compound. Since in most cases these stereoisomers could not be separated by GLC or LC, we used the NMR signal of the  $\text{CH}_2$  protons near to the carboxylic group to distinguish between *E* and *Z* forms, the  $\text{CH}_2$  signal for disubstituted *Z*-isomers appearing at lower fields than those for *E*-isomers. For example, methyl-(3*E*,6*E*)-octadienoate [1] gives a doublet at  $\delta 3.04$  ( $J_{2,3}$  6.2 Hz), whereas the 3*Z*,3*E* isomer gives a doublet at  $\delta 3.09$  ( $J_{2,3}$  5.2 Hz). Similar behaviour was observed with 3-alkenoic acids [6,7].

In the case of trisubstituted double bonds (compound XIV), we used the signal of the 4-methyl group to distinguish between the 3*E* and 3*Z* forms. The signals for the 4-methyl protons appear at lower field for the 3*Z* than for the 3*E* forms (tentative assignment; see also [8]).

Compounds V and VIII were hydrogenated over Pd/C and the products compared with authentic samples of nonanoic and dodecanoic acids, respectively. Hydrogenated compounds VI, VII, X, and XII proved to be identical with those described in the literature [9–12].

By-products XI and XIII were not isolated. From their mass spectra and GLC examination of their hydrogenated derivatives they must be taken to be allylic isomers of X and XII, respectively.

(3*Z*,6*Z*)-Dienoic acids have been reported to give signals from the double bond protons at  $\delta 5.25$  [13]. In our case the resonances are at lower fields. We were unable to detect the 6*Z* forms. The preferential formation of 6*E* compounds is consistent with the way in which they are formed (see Discussion).

Compounds VI and VII could not be separated from each other by preparative GLC, but the 3*Z*,6*E* and the 3*E*,6*E* mixtures of VI + VII were isolated. The NMR data are in full agreement with the proposed structures. Thus the  $\text{CH}_2\text{COOH}$  protons of the 3*Z*,6*E* mixture absorbed at  $\delta 3.08$ – $3.10$  (m) and the 3*E*,6*E* one at  $\delta 3.01$  (m). The four  $\text{CH}=\text{protons}$  showed signals at  $\delta 5.38$ – $5.41$  (m, 3*Z*,6*E*) and  $5.34$ – $5.49$  (m, 3*E*,6*E*). The tertiary  $\text{CH}$  gave signals (m) at  $\delta 3.04$ – $3.06$  and  $2.80$ – $2.90$  (3*Z*,6*E*) and at  $2.80$ – $2.90$  and  $2.45$ – $2.55$  (3*E*,6*E*). Other signals (3*E*,6*E* in brackets):  $1.64$  (d,  $J$  2.8 Hz),  $[1.66, \text{d}, J$  2.9 Hz],  $\text{CH}_3\text{CH}=\text{}$ ;  $1.35$ – $1.42$  (m),  $[1.37, \text{m}]$ ,  $\text{CH}_3\text{CH}_2$  of VI;  $0.84$  (t,  $J$  7.3 Hz)  $[0.85, \text{t}, J = 7.3 \text{ Hz}]$ ,  $\text{CH}_3\text{CH}_2$  of VI;  $1.99$  (m),  $[2.00, \text{m}]$

TABLE 5  
<sup>1</sup>H NMR PROPERTIES OF NEW DIENOIC ACIDS AND ESTERS (δ (ppm) rel. to TMS)

	a	b	c	d	e	f	g
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2=\text{CHCH}=\text{CHCH}_2\text{COOCH}_3 \\ \text{d} \quad \text{b} \quad \text{c} \quad \text{b} \quad \text{b} \quad \text{a} \quad \text{f} \end{array}$	3.08m 3.00m	5.27-5.81m	2.70-2.88m	4.85-5.00m	1.04-1.26(2d)	3.66s 3.67s	
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}_2\text{COOCH}_3 \\ \text{d} \quad \text{b} \quad \text{c} \quad \text{b} \quad \text{b} \quad \text{a} \quad \text{f} \end{array}$	3.07- 3.12m	5.38-5.49m	3.00-3.05m	1.64d J 4.9 Hz	1.04d J 6.7 Hz	3.68s	
$\begin{array}{c} \text{CH}_3 \\   \\ (\text{CH}_3\text{CH}=\text{CHCH}_2)_2\text{CH}=\text{CHCH}_2\text{COOH} \\ \text{d} \quad \text{b} \quad \text{b} \quad \text{c} \quad \text{b} \quad \text{b} \quad \text{a} \end{array}$	3.03d J 5.0 Hz	5.34-5.55m	2.81-2.94m	1.74d J 4.0 Hz	1.15d J 6.9 Hz	3.71s	
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH}=\text{CHCH}_2\text{C}=\text{CHCH}_2\text{COOCH}_3^a \\ \text{e} \quad \text{d} \quad \text{c} \quad \text{b} \quad \text{a} \quad \text{b} \quad \text{g} \end{array}$	3.00d J 7.0 Hz	5.33t J 7.0 Hz	2.68d J 6.0 Hz	5.23-5.52m	1.66d J 6.6 Hz	1.72s	3.66s
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH}=\text{CHCH}_2\text{C}=\text{CHCH}_2\text{COOH} \\ \text{e} \quad \text{d} \quad \text{c} \quad \text{b} \quad \text{a} \end{array}$	3.00d J 7.0 Hz	5.29t J 7.0 Hz	2.63-2.71m	5.23-5.52m	1.67d J 4.9 Hz	1.61s	3.67s
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH}=\text{CHCH}_2\text{C}=\text{CHCH}_2\text{COOH} \\ \text{e} \quad \text{d} \quad \text{c} \quad \text{b} \quad \text{a} \end{array}$	5.60d J 15.8 Hz	7.10d J 15.8 Hz	2.04d J 7.1 Hz	5.25-5.55m	1.65d J 5.7 Hz	1.04s	

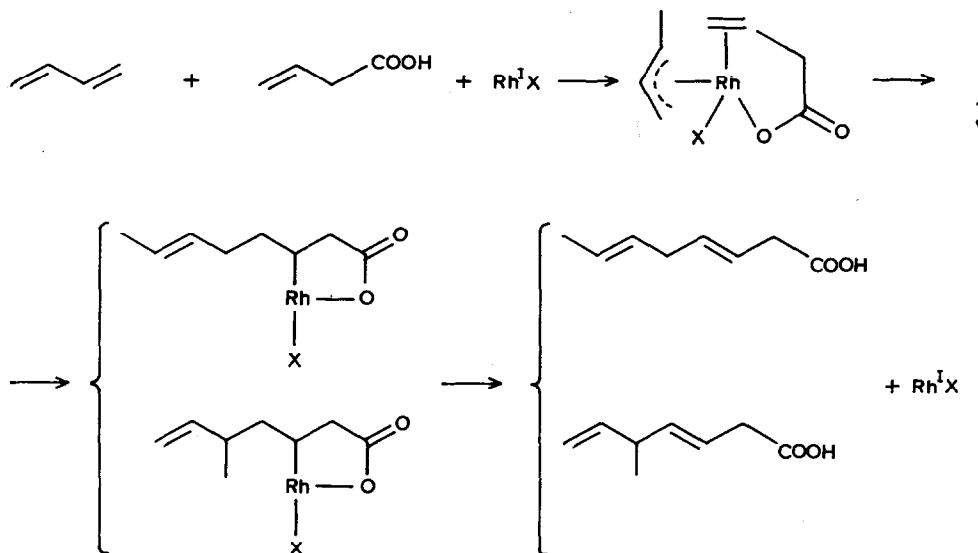
<sup>a</sup> The assignment of 3Z rather than 3E configuration is tentative.

$\text{CH}_3\text{CH}_2$  of VII; 0.96 (t,  $J$  7.4 Hz), [0.97, t,  $J$  7.3 Hz],  $\text{CH}_3\text{CH}_2$  of VII; 1.04 (d,  $J$  6.7 Hz) [1.07, d,  $J$  6.9 Hz],  $\text{CH}_3\text{CH}$  of VII.

NMR data for compounds II, IV, IX, XIV and XV, which were isolated as single stereoisomers or as mixtures of 3*Z*,6*E* and 3*E*,6*E* stereoisomers, are listed in Table 5.

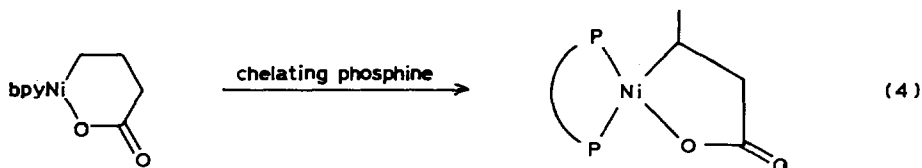
### Discussion

The features of the reaction can be interpreted in terms of Scheme 1, involving oxidative addition of 3-butenic acid to the metal ( $X = \text{Cl}$  or other anions; only *E* forms are shown; phosphorus ligands are omitted). Acids are known to add oxidatively to metals [14a]. The proton originally belonging to the acid going with the diene to form a rhodium-coordinated allylic group, which then migrates on to the butenoic double bond.



SCHEME 1

The proposal that a rhodacycle intermediate is responsible for the high regioselectivity observed is supported by the recent observation by Yamamoto et al. [14b] relating to the tendency of the product of oxidative addition of 3-butenic acid to nickel to contract to a five-membered ring (eq. 4, bpy = 2,2'-bipyridyl):



We previously reported that nickel is also active in the butadiene–butenoic acid coupling process [1].

The tendency to form the five-membered ring is so strong that 4-pentenoic acid reacts only after isomerization to 3-pentenoic acid in spite of the much higher steric hindrance at the coupling site.

It is noteworthy that the high regioselectivity observed in coupling 3-alkenoic acids with dienes is essentially due to the presence of the chelating ring. Analogous reactions of dienes with olefins mainly give mixtures, containing mostly the branched product resulting from attack at the internal position of the olefinic double bond [15].

The diene moiety reacts at the two allylic carbon atoms formed by protonation of (or rhodium hydride addition to) the diene. For steric reasons reaction at the allylic carbon which gives rise to a linear chain is generally preferred in the case of unsymmetrically substituted allyls.

Assuming allylrhodium complexes as intermediates has the implication that equilibration between  $\eta^1$  forms via the  $\eta^3$  form can occur. This process generally results in the formation of the more thermodynamically stable isomer, which is the *syn* one if a terminal alkyl substituent is present (see for example [16]). In fact the 6-double bond in the final product of our reaction generally turns out to be *E*.

The reaction appears to be quite susceptible to steric effects: yields and catalytic efficiencies fall along an homologous series of dienes or 3-alkenoic acids. It is interesting to note, however, that when branching at the C-C coupling site is involved a high selectivity can be obtained, as in the case of 3-pentenoic and 4-methyl-3-pentenoic acids (Table 2).

Beside being influenced by the C-C coupling site, the allylic moiety can also be induced to give more of the linear product by appropriate choice of the type of complex used. Cationic rhodium complexes seem to be the most effective in this respect, almost 93% linearity being attained (Table 3). An excess of phosphine ligand appears to equalize the behaviour of cationic and neutral rhodium complexes.

Variation of ligands has a remarkable effect on the reaction but no satisfactory rationalization for this has been found so far. It can only be observed that with similar electronic parameters lower conic angles are associated with higher catalytic efficiency.

Catalyst inactivation deserves some comment. Although  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  is active as catalyst the presence of gaseous CO deactivates the catalyst; thus either CO dissociation is blocked or  $\text{PPh}_3$  is replaced by CO with complete deactivation. Carbon monoxide is formed by decarbonylation of the carboxylic acids, in a known type of reaction [17].

Another source of progressive deactivation is provided by 2-alkenoic acids, which may be formed by slow isomerization of some 3-alkenoic acid, particularly 3-butenic acids. These acids must give coordination complexes which are too stable.

In conclusion, the reaction of 1,3-dienes with 3-alkenoic acids appears to proceed catalytically in the presence of rhodium(I) complexes. The reaction is very sensitive to steric effects. In some cases very high regioselectivities can be obtained. The catalytic activity can be very low in the case of species which coordinate too strongly to rhodium, but in the simplest case, involving butadiene and 3-butenic acid very high activities are observed.

## Experimental

The starting compounds were mostly commercial products (C. Erba, Fluka, Aldrich and Strem). 4-Methyl-3-pentenoic acid [18], 1,3,7-octatriene [19], 3,7-dimethyloctanoic acid [20],  $\text{Rh}(\text{COD})(\text{PPh}_3)_2\text{PF}_6$  [21],  $\text{RhH}(\text{PPh}_3)_4$  [22] and  $\text{Rh}(\text{CH}_3\text{COO})(\text{PPh}_3)_3$  [23] were prepared by published methods.



The products were analyzed by GLC on a capillary SE 52 (silicone) column by use of an internal standard, and were separated on a UCC 982 (10% silicone on Chromosorb) column.

Mass spectra were determined with a Varian CH5 instrument (70 eV).  $^1\text{H}$  NMR spectra were recorded on a Varian XL100 (compound IX) and on a Bruker WM 300 (all the other compounds) instruments. IR spectra were recorded on a Perkin-Elmer model 377 instrument.

#### *General procedure*

The unsaturated acids, the 1,3-diolefins (in excess over the stoichiometric ratio), and the catalyst were placed in a glass autoclave (100 ml) under nitrogen and kept at 120°C for 14 h with magnetic stirring. Conventional treatment yielded an acid portion, the components of which were separated by distillation and GLC.

#### **Acknowledgement**

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