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Multiple pathways in rhodium-catalyzed reactions of 1-alkynes with 3-butenoic acid *

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Abstract

Rhodium(I) complexes have been shown to catalyze the reaction of 1-alkynes with 3-butenoic acid in alcoholic solvents at 85 °C. Various pathways, involving rhodium-bonded vinylidene, α-vinyl, β-vinyl or alkynyl groups as intermediates, have been uncovered under slightly different conditions. The stereo- and regiochemisty of these reactions provide evidence for the intermediacy of vinylidene-rhodium complexes when tertiary phosphine ligands are used. Subsequent protonation leads to β-vinylrhodium complexes. In contrast, α-vinylrhodium intermediates are involved in the case of di- or tri-alkyl or -aryl-phosphite ligands. The latter ligands also favour the formation of alkynylrhodium complexes at lower temperatures. Some mechanistic aspects are discussed.

Introduction

Studies of the organometallic chemistry of alkynes have revealed a large variety of coordination modes to transition metals [1]. This suggests that a corresponding variety of catalytic reactions of coordinated alkynes should be found if the complexes used do not form too stable species with alkynes. We report here on the various pathways observed in rhodium-catalyzed organic syntheses involving 1-alkynes.

We previously described [2] the reaction of arylacetylenes with a mixture of 3-butenoic acid and its potassium salt in the presence of $RhCl(PPh_3)_3$ in ethyl

* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

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alcohol at 85 °C. Stereoisomeric dienoic acids 3-*E*-5-*Z*, 3-*Z*-5-*Z*, 3-*Z*-5-*E* and 3-*E*-5-*E* were formed non-stereoselectively (32/22/15/31 molar ratio, respectively) (eq. 1, R = aryl), together with other products derived from double addition to the alkyne (eq. 2 and 3).

$$RC{\equiv}CH + CH_2{=}CHCH_2COOH \xrightarrow{\text{Rh cat.}} RCH{=}CHCH{=}CHCH_2COOH \quad (1)$$

(I)

$$RC{\equiv}CH + 2CH_2{=}CHCH_2COOH \xrightarrow{\text{Rh cat.}}$$

$$RCH{=}\underset{\displaystyle CH_2CH_2CH_2COOH}{\underset{|}{C}}{-}CH{=}CHCH_2COOH + RCH{=}\underset{\displaystyle H_3CCHCH_2COOH}{\underset{|}{C}}{-}CH{=}CHCH_2COOH \quad (2)$$

(II) (III)

$$2RC{\equiv}CH + CH_2{=}CHCH_2COOH \xrightarrow{\text{Rh cat.}} RCH{=}\underset{\displaystyle CH_2CH_2CH_2COOH}{\underset{|}{C}}{-}C{\equiv}CR \quad (3)$$

(IV)

We suggested that the reaction path involves a rhodium-bonded carbene intermediate RCH=C=RhCl. Complexes of this type, containing triisopropylphosphine as ligand, were prepared from phenylacetylene by Werner [3]. Further support for our suggestion came from Liebeskind's reaction of phenylacetylene with a maleoylcobalt complex [4]. This reaction gave both a quinone and a fulvene derivative, and the formation of the latter was explained in terms of the intermediacy of the phenylacetylene-derived carbene. On the other hand we were able to rule out some alternative pathways by ascertaining that the monobasic acids did not result from isomerization of $PhC{\equiv}CCH_2CH_2CH_2COOH$ and that reaction 3 did not involve formation of PhCH=CHC≡CPh or PhC≡CC≡CPh. We also found that the use of a cationic rhodium complex gave the 3-*E*-5-*Z* stereoisomer of I predominantly. Further studies revealed new pathways, on which we now report.

Results

The reaction of phenylacetylene with 3-butenoic acid in ethyl alcohol at 85 °C in the presence of a rhodium(I) cationic complex $[(Rh(COD)(PPh_3)_2]PF_6$ ($+PPh_3$ in excess, COD = 1,5-cyclooctadiene), and in the absence of neutralizing agents, was found to give compounds I (3-*E*-5-*Z*) and I (3-*Z*-5-*Z*) (ca. 75/25), together with small amounts of branched isomers, resulting from attack on the internal alkyne carbon (V–VII, see below). The amount of the latter could be reduced by adding up to a 20 molar excess of triphenylphospine to the rhodium complex. The total yield increased correspondingly. The reaction was also extended to monoalkylacetylenes. Yields were rather low (up to 45%) owing to further reactions of the alkyne to give polymers and heavy products that could not be characterized (Table 1).

Addition of potassium butenoate to the starting materials resulted in the same non-stereoselective reaction observed with $RhCl(PPh_3)_3$.

Table 1

Reactions of 3-butenoic acid with alkynes in the presence of $[Rh(COD)(PPh_3)_2]^+ PF_6^-$ in EtOH, *T* 85 °C, time 24 h, butenoic acid : alkyne : Rh molar ratio = 200/100/1, [Rh] = $10^{-3}M$

Alkyne	Mol PPh_3 added per mol of Rh^+ complex	Alkyne Conversion (%)	Yield of I [a] (%)	Linear/ Branched acids	I (3-*E*-5-*Z*) Selectivity [b]
PhC≡CH	4	99	37	94/6	80
	20	99	40	97/3	72
n-C_4H_9C≡CH	0	36	7	73/27	48
	1	71	23	95/5	77
	4	84	33	99/1	77
	10	88	33	95/5	76
	20	85	40	97/3	73
	20	90	45	99/1	75 [c]

[a] Yield based on the alkyne; the linear acid (I) and branched (V–VII) acids were present in all the relevant isomeric forms; their ratio was determined by GLC of the methyl esters after hydrogenation on Pd/C; polymers and heavy products which do not show up in the GLC are also formed; the excess of butenoic acid was recovered in part as crotonic acid. [b] Selectivity on the total isomeric acids; the remaining linear acid essentially is 3-*Z*-5-*Z*. [c] Complex $[Rh(COD)(PPh_3)_2]^+ PF_6^- + 2PPh_3$ was kept in ethanol for 5–6 h under H_2, then ethylene was passed into the solution.

The use of more strongly donating phosphines (triisopropyl or tributylphosphine) lowered the yield remarkably and made the reaction much less selective.

When 1-alkynes were treated with butenoic acid and potassium butenoate in the presence of a covalent rhodium(I) complex containing trialkyl or triaryl phosphite ligands, the course of the reaction was completely changed, and branched acids (eq. 4, R = alkyl or aryl, R′ = alkyl with one less C when R = primary alkyl) were predominantly formed:

$$RC{\equiv}CH + CH_2{=}CHCH_2COOH \xrightarrow{\text{Rh cat.}}$$

$$R{-}\underset{\displaystyle CH_2}{\overset{\displaystyle \|}{C}}{-}CH{=}CHCH_2COOH + R{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CHCH{=}CHCOOH$$

(V) (VI)

$$+ R'CH{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}CH{=}CHCH_2COOH + R{-}\underset{\displaystyle CH_2}{\overset{\displaystyle \|}{C}}CH_2CH{=}CHCOOH \qquad (4)$$

(VIa) (VII)

Mixtures of *E*,*Z*-isomers were obtained in yields which did not exceed 57%, mainly owing to the formation of intractable polymers and heavy products. Monoarylacetylenes as well as monoalkylacetylenes proved to be reactive.

We ascertained that in the reaction medium one of the phosphite alkyl or aryl groups was esterified by the added acid to give a butenoic ester and dialkyl or diaryl phosphites. The latter proved to be more efficient ligands than the original triesters, as shown in Tables 2–4.

Table 2

Reactions of 3-butenoic acid and potassium 3-butenoate with alkynes in the presence of $\frac{1}{2}[RhCl(COD)]_2$ +2 mol of phosphite esters in EtOH, butenoic acid: potassium butenoate: alkyne/Rh molar ratio = 125/75/100/1, *T* 85 °C, 24 h.

Alkyne	Phosphite ester	Alkyne Conversion (%)	Total yield of isomeric acids [a]	
			Branched acids (%)	Linear acids (%)
PhC≡CH	$(PhO)_2PHO$	90	42.3	2.7
	$(PhO)_2PHO$ [b]	90	38.1	2.9
	$(i\text{-}PrO)_2PHO$	96	33.0	1.0
	$(EtO)_2PHO$	81	24.5	2.0
	$(MeO)_2PHO$	92	35.6	8.9
	$(PhO)_3P$	62	8.3	3.2
	$(i\text{-}PrO)_3P$	67	19.9	0.6
	$(EtO)_3P$	45	3.8	0.5
n-C_4H_9C≡CH	$(PhO)_2PHO$	88	51.3	2.7
	$(i\text{-}PrO)_2PHO$	97	55.2	2.3
	$(i\text{-}PrO)_2PHO$ [b]	95	49.5	2.5
	$(EtO)_2PHO$	97	55.5	2.3
	$(MeO)_2PHO$	96	53.8	2.2
	$(PhO)_3P$ [c]	93	9.0	2.3
	$(i\text{-}PrO)_3P$	65	14.5	0.5
n-C_6H_{13}C≡CH	$(EtO)_2PHO$	90	57.1	3.0
	$(i\text{-}PrO)_3P$	85	32.5	1.0
n-C_8H_{17}C≡CH	$(EtO)_2PHO$	93	55.1	2.9
	$(i\text{-}PrO)_3P$	80	34.5	1.1

[a] Yield based on the alkyne; the branched and linear acids were present in all the relevant isomeric forms (I, V–IX); their ratio was determined after hydrogenation of the methyl esters on Pd/C. Isomers distribution is shown in Table 3; polymers and heavy products which do not show up in the GLC are also formed; the excess of butenoic acid was recovered in part as crotonic acid. [b] 3 mol of phosphite added. [c] Preformed complex $RhCl[P(OPh)_3]_3$.

A secondary reaction leading to acetylenic acids was also observed (eq. 5):

$$RC{\equiv}CH + CH_2{=}CHCH_2COOH \xrightarrow{\text{Rh cat.}}$$

$$RC{\equiv}CCH_2CH_2CH_2COOH + RC{\equiv}C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2COOH \quad (5)$$

(VIII) (IX)

The product distributions at 85 °C are shown in Tables 3 and 4 for phenylacetylene and 1-hexyne respectively. 1-Octyne and 1-decyne gave a similar product distribution. It is noteworthy that the butenoic moiety always inserts in linear form when the vinyl group is formed from alkynes, but it is found partly in branched form when the reaction involves an alkynyl group. The formation of VIII was more pronounced at lower temperature (65 °C), particularly in the presence of dimethyl phosphite. The following results were obtained by reacting phenylacetylene, butenoic acid and potassium butenoate with dimethyl phosphite as ligand (P/Rh molar ratio = 3) at 65 °C for 72 h: Conversion 39%; yield%: VIII 18.8, IX 0.6, V 3.0

Table 3

Distribution of acid products from the reaction of phenylacetylene with 3-butenoic acid (%) in the presence of phosphites [a]

Phosphite ester	CH_2=C(Ph) CH=$CHCH_2$ COOH V (3-*Z*)	CH_2=C(Ph) CH=$CHCH_2$ COOH V (3-*E*)	CH_2=C(Ph) CH_2CH=CH COOH VII (2-*E*)	PhC≡CH (Me)CH_2 COOH IX	PhC≡CCH_2 CH_2CH_2 COOH VIII	PhC(Me)=CH CH=CH COOH VI (2-*Z*)	PhC(Me)=CH CH=CH COOH VI (2-*E*)	Other acids [b]
$P(OPh)_3$	19.1	23.8	11.1	7.7	8.4	8.8	1.7	19.4
$P(OPr^i)_3$	21.6	32.0	25.4	7.9	< 0.3	6.5	3.8	2.4
$P(OEt)_3$	16.3	27.6	10.7	15.4	4.6	8.5	9.7	7.2
$(PhO)_2PHO$	14.6	32.2	18.5	4.1	0.3	14.3	10.2	5.7
$(Pro^i)_2PHO$	26.8	45.6	23.2	< 0.5	< 0.5	< 0.5	< 0.5	2.5
$(EtO)_2PHO$	25.5	37.1	20.5	4.0	4.5	2.1	3.2	3.1
$(MeO)_2PHO$	17.4	34.6	14.4	6.4	14.5	2.3	4.8	5.6

[a] % GLC areas of the methyl esters. [b] Mainly I stereoisomers.

Table 4

Distribution of acid products from the reaction of 1-hexyne with 3-butenoic acid (%) in the presence of phosphites [a]

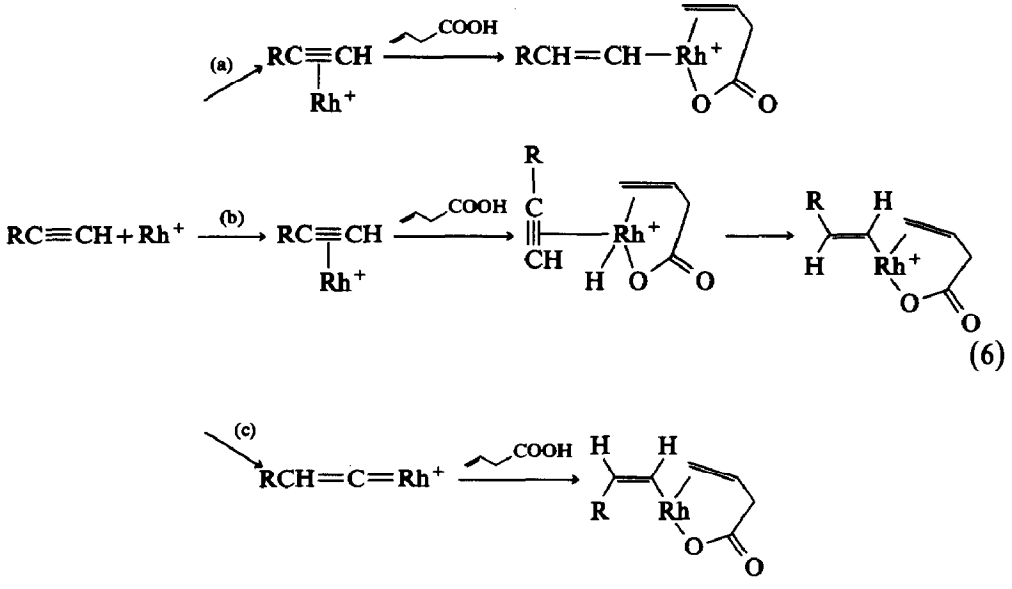
Phosphite ester	CH_2=C(Bu)CH=CH CH_2COOH V (3-*Z*)	PrCH=C(Me)CH=CH CH_2COOH VIa (3-*Z*)	CH_2=C(Bu)CH=CH CH_2COOH V (3-*E*)	PrCH=C(Me)CH=CH CH_2COOH VIa (3-*E*)	BuC≡CCH(Me) CH_2COOH IX	Other acids [b]
$P(OPh)_3$	6.5	10.3	19.1	40.7	3.0	20.3
$P(OPr^i)_3$	15.0	10.2	26.3	25.6	19.5	3.3
$(PhO)_2PHO$	9.8	13.9	25.7	45.6	–	5.0
$(Pr^iO)_2PHO$	5.9	14.5	26.0	49.5	–	4.1
$(EtO)_2PHO$	4.5	10.9	35.2	45.3	–	4.1
$(MeO)_2PHO$	5.6	11.8	27.7	50.9	–	4.0

[a] % GLC areas of the methyl esters; [b] Mainly phenylhexadienoic acid stereoisomers (I).

($Z/E = 2/1$), VII(E) 0.5, I stereoisomers 1.7. Most of the acids thus consist of the alkynoic isomers. The latter are not formed when triphenylphosphine is used in place of phosphite ligands.

Discussion

On the basis of the results obtained with the cationic rhodium complex, we consider (see eq. 6; phosphine ligands are omitted) three routes to reactive rhodium-bonded species from alkynes: (a) direct protonation of the alkyne; (b) hydride addition to the alkyne; and (c) carbene formation, followed by protonation:



(6)

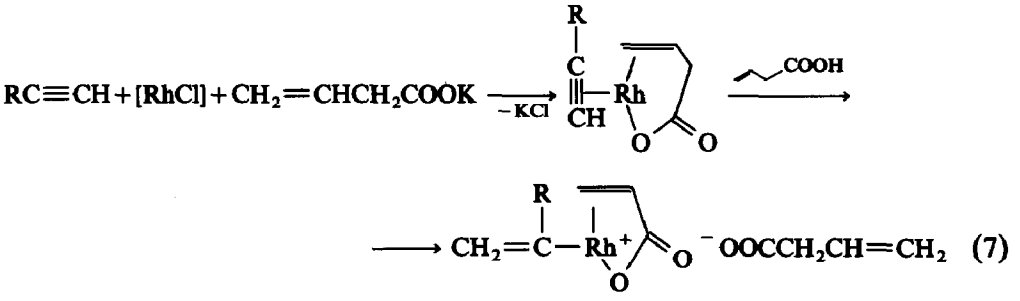
Route (a) is in conflict with the expected mode of protonation, which should give the rhodium-bonded α-styryl group and not the β one, as observed. Route (b) is not consistent with the formation of the 5-Z isomers; *cis* addition of a rhodium hydride should give the E styryl group and not the Z one. Since these reactions are stereospecific, the initial stereochemistry must be preserved in the 5-Z products. We are thus left with route (c): this route is supported by the results from Werner's protonation experiments of rhodium-bonded phenylvinylidene, which gave products with Z stereochemistry [3b].

The formation of a vinylidenerhodium complex deserves some comment. A cationic rhodium complex could favor alkyne coordination. In fact, alkylacetylenes, which had been found not to react with the neutral complex, readily reacted with the cationic one. Bianchini's results on oxidative addition of phenylacetylene to a cationic rhodium complex [5] are noteworthy in this context. Bianchini observed the formation of a hydridophenylalkynyl complex from phenylacetylene, but he did not observe hydride migration on the phenylalkynyl group to form the vinylidene complex. The latter was instead obtained by protonation of a phenylalkynyl complex. In our case we must assume that either the vinylidene complex is formed directly from the alkyne by 1,2-hydrogen shift [6] or that there is initially an

oxidative addition of the alkyne to rhodium to give a hydride (which is transformed to other species) and a rhodium-bonded alkynyl group, which is protonated to give a vinylidene by butenoic acid.

We confirmed that insertion of the double bond of the latter into the styryl–rhodium bond, formed by vinylidene protonation, took place by treating styryl bromide with Wilkinson's catalyst in the presence of potassium butenoate [2]. Although, owing to the failure of *Z*-bromostyrene to undergo oxidative addition to rhodium, only the *E*-styryl group reacted, we see no reason why, once bonded to rhodium, the *Z*-styryl group should not undergo the same insertion process as the *E* one. We also attempted to bring about C–C coupling between butenoic acid and Werner's phenylvinylidenerhodium complexes [3], but no reaction occurred, probably because the presence of triisopropylphosphine as ligand prevented coordination of the butenoic double bond, apparently a prerequisite for the occurrence of the reaction. Even so, however, the vinylidene pathway seems to be sufficiently supported by the experiments described above.

The results obtained with the rhodium-phosphite complex mean that in this case initial protonation of the alkyne is favored over vinylidenerhodium formation, and the regiochemistry is also that expected for protonation. The higher electron-withdrawing character of phosphite than of phosphine ligands favors alkyne protonation. Chloride replacement by potassium butenoate should facilitate the alkyne coordination and at the same time should favor chelation of the butenoic group (eq. 7):



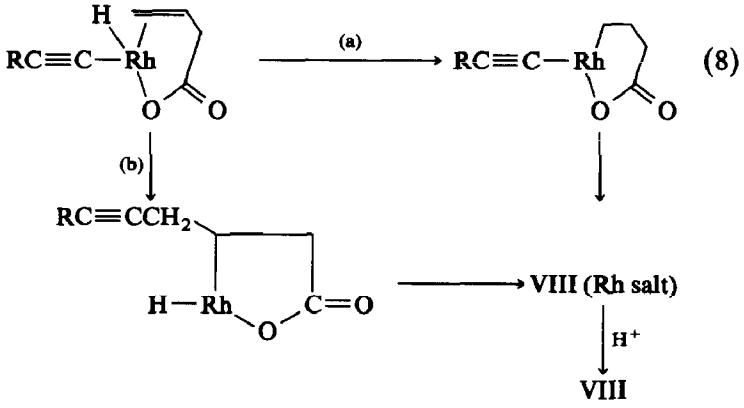
(7)

It is noteworthy that dialkyl or diaryl phosphites have proved to be more efficient ligands than the respective tertiary ones. This may be because of their lower steric hindrance and/or of their ability to undergo oxidative addition to rhodium [7]. The latter process would give a hydridorhodium phosphonate, which in the protic solvent used could act as an efficient protonation agent for the alkyne. In the presence of butenoic acid regeneration of the dialkyl or diaryl phosphite would follow, so that this ligand would behave catalytically.

The formation of alkynoic acids under the same conditions (phosphite ligands, potassium butenoate/butenoic acid) suggests that there is preliminary formation of an alkynylrhodium hydride. The hydride, however, does not migrate to the alkyne, but directly or indirectly (e.g. by phosphite assistance, as just mentioned), moves onto the butenoic chain (eq. 8, path (a), thus forming a rhodacycle able to couple

with the alkynyl group. The preparation of a metallacycle from butenoic acid was reported by Yamamoto in the case of nickel [8].

$$RC{\equiv}CH + [RhCl] + CH_2{=}CHCH_2COOK \longrightarrow$$

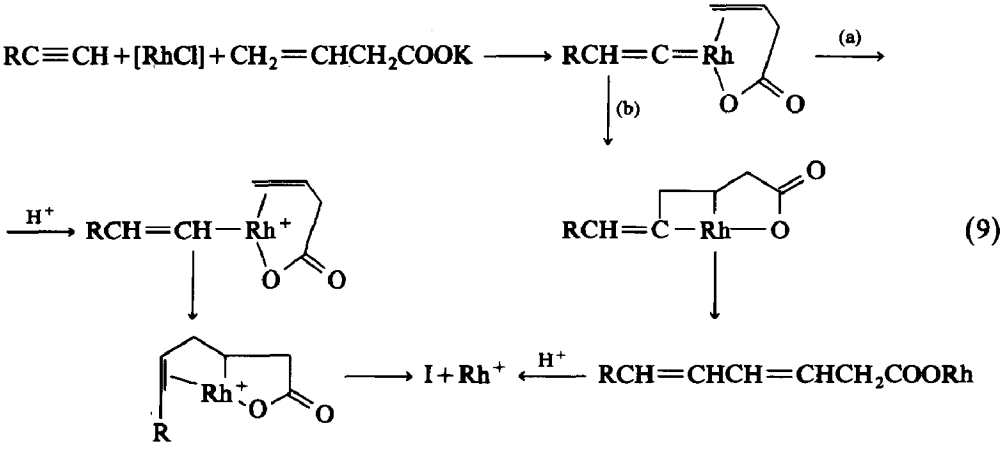


(8)

Route (b) seems less likely for two reasons: (1) the alkynyl group migrates rather reluctantly [9*]; (2) contrary to what is observed, an insertion reaction should lead exclusively to a linear butenoic chain [10].

Analogous pathways must operate for compound IX.

On the basis of these facts the behaviour of the neutral rhodium complex containing phosphines (Wilkinson's catalyst) in the presence of butenoic acid and potassium butenoate, as described previously [2], can be represented as follows (eq. 9):



(9)

In the presence of phosphines as ligands the rhodium-bonded vinylidene should be readily formed. At this point it has two possible ways, (a) and (b), to the final product.

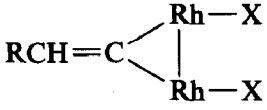
Route (a) is similar to that postulated above for the reaction of the cationic rhodium complex. This is in accord with the fact that addition to potassium butenoate to the reaction solution, containing the cationic rhodium complex gave the same results as those found with Wilkinson's catalyst. There is a difficulty however, in respect of the absence of stereoselectivity of this reaction, which

* Reference number with asterisk indicates a note in the list of references

contrasts with the high stereoselectivity obtained with the cationic rhodium complex. It seems reasonable, however, that a *Z* to *E* isomerization of the rhodium-bonded styryl group takes place, and such isomerization has been observed by Werner [3b]. On the other hand we ascertained that the *E,Z* product formed in the presence of the cationic complex does not isomerize under the conditions used with Wilkinson's, so the only stage at which an isomerization can take place is that at which there is a styryl-rhodium bond. The reason why isomerization does not occur under the conditions used with the cationic complex (eq. 6, Route (c)) must be that there is a fast insertion of the butenoic double bond, so that there is no time for *Z* to *E* isomerization.

Route (b), involving metallocyclobutane formation, is another possibility. That metallacyclobutanes, formed by addition of a metal-coordinated carbene to an olefins, can decompose to a new olefinic compound by loss of hydrogen, without giving metathesis products has been shown by Semmelhack [11] in the case of a Fischer-type carbene complex.

The main reason for favouring route (b) is that the rhodacyclic intermediate shown above could undergo further incorporation of either the alkyne or butenoic acid to give the secondary products II–IV by ring enlargement. In contrast compounds II–IV are not formed with cationic rhodium complexes. As an alternative interpretation of this behaviour, however, it is possible that neutral complexes favor further addition because they are converted into dimers of type X (X = butenoate), which could undergo double addition more easily.



(X)

A rhodium carbonyl complex of this type (R = H, X = indenyl) has been described [12]. Further work is in progress to clarify this point.

In conclusion, it has been shown that alkynes can react with rhodium complexes in the form of vinylidene carbenes, alkynyl groups or vinyl groups. The reaction of these species with the chelating double bond of butenoic acid leads to a wide range of unsaturated acids. The proposed course of these reactions is supported by the regio and stereochemistry and by previously reported stoichiometric reactions on organometallic complexes. Further work is required, however, to clarify the nature of the organometallic intermediates involved.

Experimental

Starting materials were commercial products (Aldrich and Strem). Rhodium complexes were prepared by published procedures [13–15].

Products were analyzed by GLC on a capillary SE 52 (silicone) column and separated on a UCC 982 (10% silicone on Chromosorb) column. Mass spectra were obtained with a Varian CH5 instrument (70 eV) and ^{1}H NMR spectra were recorded on Varian XL-100 and Bruker WM 300 instruments.

General procedure for the synthesis of 6-substituted 3,5-hexadienoic acids

A magnetically stirred solution of the catalyst ($[Rh(COD)(PPh_3)_2]PF_6$, with or without an excess of triphenylphospine), 3-butenoic acid, and the alkyne in

Table 5

NMR data for the methyl esters of new compounds

		a	b, b′	c	d	e	e′	f	g	h	i
CH_2=C(Ph)CH=$CHCH_2COOCH_3$	3-*Z*	3.72 s	3.89 d	6.24 dt	5.82 dt	5.38 s	5.10 s				
ee′ d c b a			*J* 7.2	*J* 7.2	*J* 11.4						
(V)				*J* 11.4	*J* 1.9						
	3-*E*	3.71 s	3.18 d	5.75 dt	6.41 d	5.25 s	5.16 s				
			J 7.0	*J* 7.5	*J* 15.0						
				J 15.0							
CH_2=C(Ph)CH_2CH=$CHCOOCH_3$	2-*E*	3.71 s	5.89 dt	7.05 dt	3.39 dt	5.47 s	5.10 s				
ee′ d c b a			*J* 15.6	*J* 15.6	*J* 6.7						
(VII)			*J* 1.6	*J* 6.7	*J* 1.6						
PhC(CH_3)=CHCH=$CHCOOCH_3$	2-*Z*	3.75 s	5.76 d	7.07 t	7.88 d	2.27 d					
e d c b a			*J* 11.6	*J* 11.6	*J* 11.6	*J* 1.0					
(VI)											
	2-*E*	3.78 s	5.98 d	7.75 dd	6.57 d	2.31 d					
			J 15.1	*J* 15.2	*J* 11.8	*J* 1.0					
				J 11.8							
PhC≡$CCH_2CH_2CH_2COOCH_3$		3.62 s	2.45 t [a]	1.89 quintet	2.47 t [a]						
d c b a			*J* 7.4	*J* 7.4	*J* 7.4						
(VIII)											
PhC≡$CCH(CH_3)CH_2COOCH_3$		3.57 s	2.24 dd	3.00–3.16 m	1.04 d						
c d b, b′ a			J_{vic} 5.15		*J* 7.2						
(IX)			J_{gem} 17.0								
			b′ 2.72 dd								
			J_{vic} 9.07								
			J_{gem} 17.0								

ee′ CH_2 $CH_3CH_2CH_2CH_2CCH{=}CHCH_2COOCH_3$ i h g f d c b a (V)	3-*Z*	3.67 s	3.06d *J* 7.5	5.66 dt *J* 7.5 *J* 11.0	5.97 d *J* 11.0	4.81 s	4.99 s	2.04 t *J* 7.5	1.15–1.46 m	0.90 t *J* 7.4
ee′ CH_2 $CH_3CH_2CH_2CH_2CCH{=}CHCH_2COOCH_3$ i h g f d c b a	3-*E*	3.68 s	3.12 d *J* 7.3	5.76 dt *J* 15.8 *J* 7.3	6.13 d *J* 15.8	4.92 s	4.92 s	2.18 t *J* 7.5	1.20–1.50 m	0.90 t *J* 7.3
e CH_3 $CH_3CH_2CH_2CH_2{\equiv}CCHCH_2COOCH_3$ h g f d, d′ c b, b′ a (IX)		3.63 s	2.26 dd J_{vic} 5.3 J_{gem} 16.8 b′2.76 dd J_{vic} 8.8 J_{gem} 16.8	2.92–3.08 m	2.49 t *J* 7.2 d′2.50 t *J* 7.6	1.10 d *J* 7.3		1.56 quintet *J* 7.3	1.18–1.37 m	0.87 t *J* 6.9

[a] b and d may correspond to d and b.

1/200/100 molar ratio in ethyl alcohol ([Rh] = 10^{-3} *M*) was kept under nitrogen at 85 °C for 24 h in an oil bath. The mixture obtained was separated by conventional acid-base treatment, then esterified with diazomethane, analyzed by GLC/MS, and then separated into the single components by preparative GC.

General procedure for the synthesis of 5-substituted 3,5- or 2,5-hexadienoic acids

A solution of the catalyst (prepared from $[RhCl(COD)]_2$ and a 2 or 3 equivalent proportion of the phosphite ester), 3-butenoic acid, potassium 3-butenoate, and the alkyne in a 1/125/75/1 molar ratio in ethyl alcohol was kept at 85 °C for 24 h under the same conditions described above. Work-up as above was used to give the separate products.

General procedure for the synthesis of 6-substituted 5-alkynoic acids or 5-substituted 3-methyl-4-alkynoic acids

The conditions were the same as those above except that the reaction temperature was 65 °C and the reaction time 72 h. Product separation was carried out as before.

Properties of products

Methyl esters were first characterized as hydrogenated products by MS spectrometry and NMR spectroscopy by comparison with literature data for 6-phenylhexanoic [16], 5-phenylhexanoic [17], 3-methylnonanoic, 5-methylundecanoic, 5-methyltridecanoic [18], and 3-methyl-5-pentanoic [19] acids. The NMR data for the methyl esters of new compounds are listed in Table 5. The stereochemistry at the trisubstituted double bond of VI was not determined. Isomeric methyl esters derived from 1-octyne or 1-decyne showed a GLC sequence of retention times corresponding to that observed with those from 1-hexyne. These compounds were not separated, but were converted into known compounds [18] by hydrogenation. The NMR data for the isomeric 6-phenyl-3,5-hexadienoic esters were published previously [2], as were as those for 5-methyl-3,5-nonadienoic esters [10c]. The preparation of 6-phenyl-5-hexynoic acid has been described previously [20], but no NMR data were given, so these are reported in Table 5.

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