

RHODIUM-CATALYZED C-C COUPLING OF ALLENES WITH 3-BUTENOIC ACID

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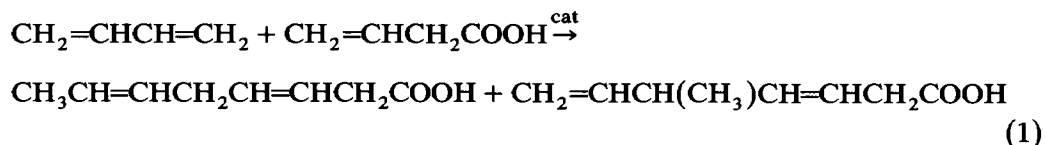
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Summary

Allenes react with 3-butenic acid under the catalytic action of rhodium(I) complexes to give dienic acids. While 3-butenic acid reacts selectively at the terminal carbon atom, allenes can react both at the central and at the terminal carbon atoms of the allenic system. The most important synthetic aspect is that, unlike terminal 1,3-dienes, higher homologues of allene can be caused to react preferentially at the terminal position, thus giving rise to linear 3,6-dienic acids. Furthermore, the regioselectivity can be reversed using phosphites as ligands in place of phosphines, the major products being branched 3,5-dienic acids.

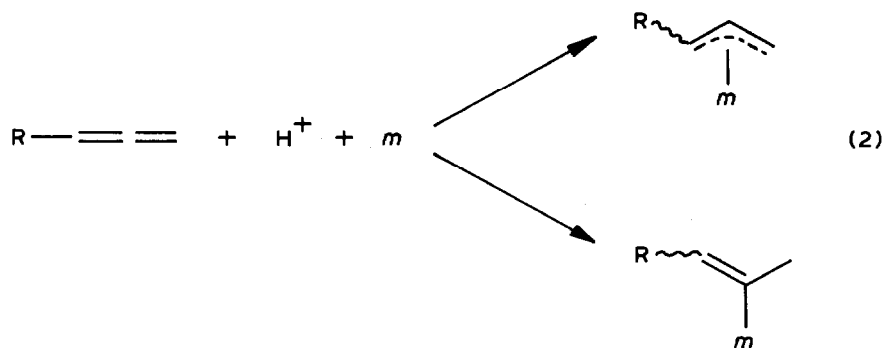
Introduction

We previously reported [1,2] that 1,3-dienes react with butenoic acids in a rhodium-catalyzed reaction, according to eq. 1 (which is written for the simplest case):



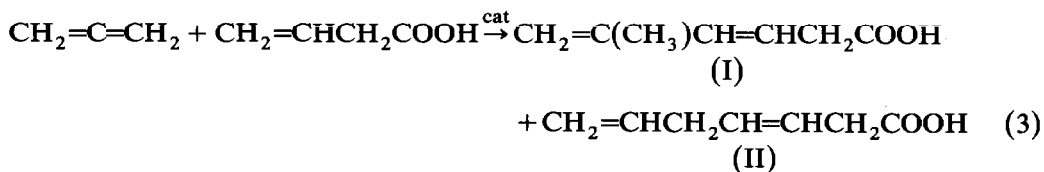
The reaction involves formation of η^3 -allylic complexes. Higher dienes mainly give substituted allyls, which afford predominantly branched dienic acids.

The present work involved a study of reactions of 1,2-dienes with 3-butenic acid. In principle 1,2-dienes could form allylic or vinylic systems (eq. 2), R = H, alkyl, aryl; m = metal complex). This offers interesting synthetic possibilities which merit exploration.



Results

The simplest 1,2-diene, allene, reacts with 3-butenic acid at 85°C in the presence of catalytic amounts of rhodium(I) complexes with phosphorus ligands according to eq. 3. The isopropenyl esters of these acids as well as those of



3-butenic acid are formed as by-products.

When an allene to catalyst ($\text{RhCl}(\text{PPh}_3)_3$) molar ratio of 800/1 and a butenoic acid to catalyst ratio of 850 are used, acids I and II are formed in a 3/1 molar ratio. Butenoic acid (55%) is isolated after 14 h of reaction. Acids I and II account for a 23% of the yield. Another 15% consists of the isopropenyl esters of butenoic acid (III) and ca. 3% of the isopropenyl ester of I and II. Two isomers of I, 3-*E* and 3-*Z*, are present in a 2/1 ratio. The 3-*E* and 3-*Z* isomers of II are also present in an approximately 1/1 ratio.

The overall catalytic efficiency is ca. 309 mol of products per mol of catalyst (186 of I + II).

Monosubstituted allenes also react with 3-butenic acid to give type I (3,5) and II (3,6) acids, but the latter are predominant. The yields are generally rather low because of the marked tendency of the allene system to give polymeric products. These compounds being neutral, however, can be readily separated from the desired acids.

The compounds obtained are listed below, with the isomer distribution (% GLC peak areas) in parentheses. Yields and molar ratios of the 3,6 : 3,5-acids are given in Table 2.

Compounds XI and XII were not isolated as such but after hydrogenation. The products were compared with authentic samples of 5-ethylundecanoic and 5-methyldodecanoic acids. The formulae in square brackets are suggested on the basis of the general information available for the other isolated compounds.

The stereochemistry of the 3-double bond was assigned, when possible, on the

TABLE 1
COMPOUNDS OBTAINED WITH ISOMER DISTRIBUTIONS IN PARENTHESES

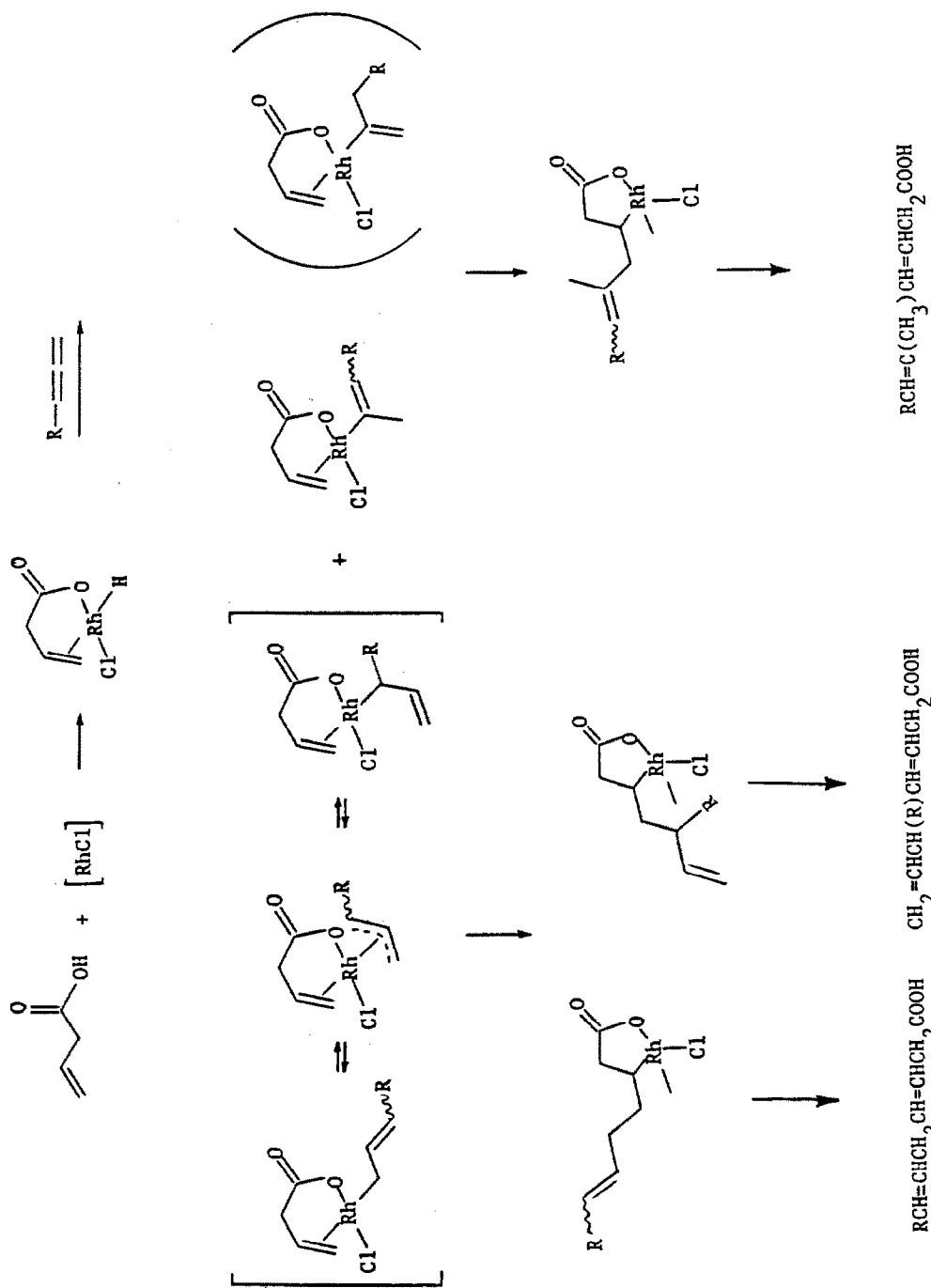
From $C_2H_5CH=C=CH_2$	$C_2H_5CH=CHCH_2CH=CHCH_2COOH$	IV	(52)
	$CH_2=CHCH(C_2H_5)CH=CHCH_2COOH$	V	(7)
	$C_2H_5CH=C(CH_3)CH=CHCH_2COOH$	VI	(41)
From $n-C_3H_7CH=C=CH_2$	$n-C_3H_7CH=CHCH_2CH=CHCH_2COOH$	VII	(73)
	$CH_2=CHCH(n-C_3H_7)CH=CHCH_2COOH$	VIII	(7)
	$n-C_3H_7CH=C(CH_3)CH=CHCH_2COOH$	IX	(20)
From $n-C_6H_{13}CH=C=CH_2$	$n-C_6H_{13}CH=CHCH_2CH=CHCH_2COOH$	X	(70)
	$[CH_2=CHCH(n-C_6H_{13})CH=CHCH_2COOH]$	XI	(2)
	$[n-C_6H_{13}CH=C(CH_3)CH=CHCH_2COOH]$	XII	(28)
From $C_6H_5CH=C=CH_2$	$C_6H_5CH=CHCH_2CH=CHCH_2COOH$	XIII	(90)
	$C_6H_5CH=C(CH_3)CH=CHCH_2COOH$	XIV	(10)
From $(CH_3)_2C=C=CH_2$	$(CH_3)_2C=CHCH_2CH=CHCH_2COOH$ [3]	XV	(90)
	$(CH_3)_2C=C(CH_3)CH=CHCH_2COOH$	XVI	(10)
From $CH_3CH=C=CHCH_3$	$CH_3CH=CHCH(CH_3)CH=CHCH_2COOH$ [2]	XVII	(85)
	$CH_3CH=C(C_2H_5)CH=CHCH_2COOH$	XVIII	(15)

basis of the coupling constant and also on the basis of the CH_2COOR signal, which generally is at lower field in the *Z* than in the corresponding *E* compounds [2]. The 3-*E*/3-*Z* ratio ranges from 1 to 2 for the 3,6-acids. This ratio is ca. 3 for the acids derived from disubstituted allene 2,3-pentadiene. In the case of 1,1-dimethylallene the ratio is ca. 2 for the 3,6-isomer. The attribution of stereochemistry to the 6-double bond is more difficult but there is little doubt that the stereochemistry is *E*. This has been clearly shown for phenylheptadienoic acid (XIII), but in the other cases also this must be the major if not the exclusive stereoisomer. In fact transition metal-catalyzed reactions involving allyl compounds with a terminal alkyl substituent generally give rise to *E* compounds, which are the thermodynamically more stable [2,4].

TABLE 2
REACTION OF 1,2-DIENES WITH 3-BUTENOIC ACID WITH $RhCl(PPh_3)_3$ AS CATALYST AT $85^\circ C$

Allene	mol allene	mol butenoic acid	t (h)	Yield of acids (%) ^a	mol dienic acids 3,6/3,5	mol acids
	mol Rh	mol Rh				mol catalyst
$CH_2=C=CH_2$	800	850	4	23.3	33/67	186
$CH_3CH_2CH=C=CH_2$	550	600	4	30.7	59/41	169
$n-C_3H_7CH=C=CH_2$	400	450	5	40.0	80/20	160
$n-C_6H_{13}CH=C=CH_2$	200	230	10	30.0	72/28	60
$C_6H_5CH=C=CH_2$	200	270	4	15.5	90/10	31
$(CH_3)_2C=C=CH_2$	500	575	5	44.0	90/10	220
$CH_3CH=C=CHCH_3$	50	70	5	32.0	75/25	16

^a Total yield of acids based on allene used up; the allene conversion was practically complete, except for the unsubstituted allene (92%). Higher allenes mainly gave polymeric products, not detectable by GLC. Most of the uncharged butenoic acid was recovered.



SCHEME 1

TABLE 3

REACTION OF 1,2-HEXADIENE (400 mmol), 3-BUTENOIC ACID (450 mmol) 1/2 RhCl(COD)₂ (1 mmol COD = 1,5 cyclooctadiene) AND LIGANDS L (4 mmol) AT 85 °C FOR 5 h

L	Yield (%) ^a	mol total acids	
		mol 3,6-dienoic acids	mol 3,5-dienoic acids
P(Ph ₃) ₃	42	80/20	167
P(O- <i>i</i> -Pr) ₃	42	6/94 ^b	169
P(OEt) ₃	17	5/95 ^b	67
P(<i>n</i> -Bu) ₃	37	18/82	149

^a Total yield of acids based on 1,2-hexadiene taken; most of butenoic acid was recovered. ^b n-C₃H₇CH=C(CH₃)C(=CH₂)CH₂COOH (IXa) is also formed in ≤ 2.5% yield and is included in 3,5-dienoic acids.

For the 3,5-isomers the 3-*E*/3-*Z* ratio is ca. 1 for the acids derived from monosubstituted allenes, whereas the acid from 1,1-dimethylallene is predominantly *E*.

The stereochemistry of the trisubstituted 5-double bonds is probably *E* in all cases except for XVIII which has been assigned 3-*E*-5-*E* and 3-*E*-5-*Z* configurations in view of the high coupling constant of both isomers (15.7 Hz). All the trisubstituted 3,5-derivatives reported here show chemical shifts of CH= below δ 6.22 ppm, whereas compound XVI, which has one of the two terminal methyl groups in the same configuration as in a 5-*Z* compound, resonates at δ 6.55 ppm, near to the value, 6.45, for XVIII. This could be taken to indicate that all the 3,5 compounds are 5-*E* except for XVIII, which is a mixture of 5-*E* and 5-*Z* (2/1); the observation [5] that 3-methyl-2,4-heptadiene resonances at 6.06 and 6.44, respectively for the *E*, *E* and *E*, *Z* isomers is in accord with this interpretation.

The use of different ligands in the rhodium complex provides control of the selectivity of the reaction towards 3,6- or 3,5-dienoic acids. As shown in Table 3 the ratio between 3,6- and 3,5-dienoic acids varies from 80/20 in the case of triphenylphosphine to 6/94 in the case of triisopropyl phosphite.

Discussion

Since experiments performed under the same conditions with 1-alkynes or with the isopropenyl ester of 3-butenoic acid failed we can rule out the possibility that these species are formed as intermediates from the allenes. We therefore assume that under the action of 3-butenoic acid the allenes are converted into allyl- or vinyl-rhodium species. 3-Butenoic acid must form a chelated ring to account for its unique reaction with butadiene, since 2 or 4 unsaturated acids are unreactive under the mild conditions used. Scheme 1 depicts the proposed course of the reaction, and involves oxidative addition of butenoic acid to the rhodium(I) complex and formation of an allyl- or vinyl-rhodium bond by reaction with allenes, followed by insertion and H-elimination.

It is worth noting that since allylrhodium complexes are preferred with triphenylphosphine as ligand, linear dienoic acids are obtained in higher proportion than with the corresponding 1,3-dienes. A clear comparison can be made in the case of

(Continued on p. 380)

TABLE 4

¹H NMR DATA FOR NEW COMPOUNDS (CDCl₃, TMS)^a

I	$\text{CH}_2=\overset{\text{d}}{\text{C}}(\overset{\text{e}}{\text{CH}_3})\overset{\text{c}}{\text{CH}}=\overset{\text{b}}{\text{CH}}\overset{\text{a}}{\text{CH}_2}\overset{\text{f}}{\text{COOCH}_3}$	Z	3.30 (d, <i>J</i> _{ab} 7.3 Hz, <i>J</i> _{ac} 1.7 Hz, 2H, H _a), 5.56–5.66 (m, 1H, H _b), 6.00 (d, <i>J</i> _{bc} 11.0 Hz, 1H, H _c), 4.85 (s, 1H, H _d), 5.01 (s, 1H, H _d), 1.85 (s, 3H, H _e), 3.69 (s, 3H, H _f)
I	$\text{CH}_2=\overset{\text{d}}{\text{C}}(\overset{\text{e}}{\text{CH}_3})\overset{\text{c}}{\text{CH}}=\overset{\text{b}}{\text{CH}}\overset{\text{a}}{\text{CH}_2}\overset{\text{f}}{\text{COOCH}_3}$	E	3.14 (d, <i>J</i> _{ab} 7.0 Hz, 1H, H _a), 5.72 (dt, <i>J</i> _{ab} 7.0 Hz, <i>J</i> _{bc} 15.9 Hz, 1H, H _b), 6.22 (d, <i>J</i> _{bc} 15.9 Hz, 1H, H _c), 4.93 (s, 1H, H _d), 4.94 (s, 1H, H _d), 1.85 (s, 3H, H _e), 3.69 (s, 3H, H _f)
III	$\overset{\text{d}}{\text{CH}_2}=\overset{\text{c}}{\text{CH}}\overset{\text{b}}{\text{CH}_2}\overset{\text{e}}{\text{COOC}}(\overset{\text{a}}{\text{CH}_3})=\overset{\text{a}}{\text{CH}_2}$		4.69 (s, 2H, H _a), 3.16 (dt, <i>J</i> _{bc} 7.0 Hz, <i>J</i> _{bd} 2.0 Hz, 2H, H _b), 5.68–6.14 (m, 1H, H _c), 5.18–5.23 (m, 2H, H _d), 1.92 (s, 3H, H _e)
IV	$\overset{\text{c}}{\text{CH}_3}\overset{\text{d}}{\text{CH}_2}\overset{\text{b}}{\text{CH}}=\overset{\text{c}}{\text{CH}}\overset{\text{b}}{\text{CH}_2}\overset{\text{a}}{\text{CH}}=\overset{\text{f}}{\text{CH}}\overset{\text{a}}{\text{CH}_2}\overset{\text{f}}{\text{COOCH}_3}$	3-Z;(6-E); 3-E;(6-E)	3.08 (d, <i>J</i> _{ab} 5.4 Hz, 2H, H _a Z), 3.02 (d, <i>J</i> _{bd} 4.9 Hz, 2H, H _a E), 5.28–5.60 (m, 4H, H _b), 2.72 (m, 2H, H _c), 2.01 (m, 2H, H _d), 0.98 (t, <i>J</i> _{ed} 7.4 Hz, 3H, H _e), 3.68 (s, 3H, H _f Z), 3.67 (s, 3H, H _f E)
V	$\overset{\text{d}}{\text{CH}_2}=\overset{\text{b}}{\text{CH}}\overset{\text{c}}{\text{CH}}(\overset{\text{e}}{\text{CH}_2}\overset{\text{f}}{\text{CH}_3})\overset{\text{b}}{\text{CH}}=\overset{\text{a}}{\text{CH}}\overset{\text{a}}{\text{CH}_2}\overset{\text{g}}{\text{COOCH}_3}$	3-Z;3-E	3.10 (d, <i>J</i> _{ab} 6.8 Hz, 2H, H _a Z), 3.05 (d, <i>J</i> _{ab} 5.9 Hz, 2H, H _a E), 5.36–5.77 (m, 3H, H _b), 2.60 (m, pseudo quintet, 1H, H _c Z), 2.86 (m, pseudo quintet, 1H, H _c E), 4.85–5.04 (m, 2H, H _d), 1.43 (m, 2H, H _e), 0.87 (t, <i>J</i> _{ef} 7.5 Hz, 3H, H _f), 3.69 (s, 3H, H _g)
VI	$\overset{\text{e}}{\text{CH}_3}\overset{\text{d}}{\text{CH}_2}\overset{\text{b}}{\text{CH}}=\overset{\text{f}}{\text{C}}(\overset{\text{c}}{\text{CH}_3})\overset{\text{c}}{\text{CH}}=\overset{\text{b}}{\text{CH}}\overset{\text{a}}{\text{CH}_2}\overset{\text{g}}{\text{COOCH}_3}$	3-Z-(5-E)	3.28 (dd, <i>J</i> _{ab} 7.3 Hz, <i>J</i> _{ac} 1.7 Hz, 2H, H _a), 5.38–5.62 (m, 2H, H _b), 5.97 (d, <i>J</i> _{bc} 11.3 Hz, 1H, H _c), 2.10 (dq, <i>J</i> _{de} 7.4 Hz, 2H, H _d), 1.00 (t, <i>J</i> _{de} 7.4 Hz, 3H, H _e), 1.74 (s, 3H, H _f), 3.69 (s, 3H, H _g)
VI	$\overset{\text{f}}{\text{CH}_3}\overset{\text{e}}{\text{CH}_2}\overset{\text{d}}{\text{CH}}=\overset{\text{g}}{\text{C}}(\overset{\text{c}}{\text{CH}_3})\overset{\text{c}}{\text{CH}}=\overset{\text{b}}{\text{CH}}\overset{\text{a}}{\text{CH}_2}\overset{\text{h}}{\text{COOCH}_3}$	3-E-(5-E)	3.11 (d, <i>J</i> _{ab} 7.1 Hz, 2H, H _a), 5.59 (dt, <i>J</i> _{bc} 15.6 Hz, <i>J</i> _{ab} 7.1 Hz, 1H, H _b), 6.11 (d, <i>J</i> _{bc} 15.6 Hz, 1H, H _c), 5.41 (t, <i>J</i> _{de} 7.1 Hz, 1H, H _d), 2.13 (dq, <i>J</i> _{de} 7.1 Hz, <i>J</i> _{ef} 7.5 Hz, 2H, H _e), 0.98 (t, <i>J</i> _{ef} 7.5 Hz, 3H, H _f), 1.74 (s, 3H, H _g), 3.68 (s, 3H, H _h)
VII	$\overset{\text{f}}{\text{CH}_3}\overset{\text{e}}{\text{CH}_2}\overset{\text{d}}{\text{CH}_2}\overset{\text{b}}{\text{CH}}=\overset{\text{c}}{\text{CH}}\overset{\text{c}}{\text{CH}_2}\overset{\text{b}}{\text{CH}}=\overset{\text{a}}{\text{CH}}\overset{\text{a}}{\text{CH}_2}\overset{\text{g}}{\text{COOCH}_3}$	3-Z-(6-E) 3-E-(6-E)	3.08 (d, <i>J</i> _{ab} 5.2 Hz, 2H, H _a Z), 3.02 (d, <i>J</i> _{ab} 5.0 Hz, 2H, H _a E), 5.28–5.59 (m, 4H, H _b), 2.68–2.80 (m, 2H, H _c), 1.89–2.03 (m, 2H, H _d), 1.28–1.50 (m, 2H, H _e), 0.88 (t, <i>J</i> _{ef} 7.3 Hz, 3H, H _f), 3.68 (s, 3H, H _g)
VIII	$\overset{\text{d}}{\text{CH}_2}=\overset{\text{b}}{\text{CH}}\overset{\text{c}}{\text{CH}}(\overset{\text{e}}{\text{CH}_2}\overset{\text{f}}{\text{CH}_3})\overset{\text{b}}{\text{CH}}=\overset{\text{a}}{\text{CH}}\overset{\text{a}}{\text{CH}_2}\overset{\text{g}}{\text{COOCH}_3}$	3-E; 3-Z	3.04 (d, <i>J</i> _{ab} 6.4 Hz, 2H, H _a Z), 3.00 (d, <i>J</i> _{ab} 5.9 Hz, 2H, H _a E), 4.87–4.98 (m, 3H, H _b), 2.69–2.92 (m, 1H, H _c), 5.22–5.71 (m, 2H, H _d), 1.20–1.41 (m, 4H, H _e), 0.87 (t, <i>J</i> _{ef} 7.5 Hz, 3H, H _f), 3.67 (s, 3H, H _g)
IX	$\overset{\text{g}}{\text{CH}_3}\overset{\text{f}}{\text{CH}_2}\overset{\text{e}}{\text{CH}_2}\overset{\text{d}}{\text{CH}}=\overset{\text{h}}{\text{C}}(\overset{\text{c}}{\text{CH}_3})\overset{\text{c}}{\text{CH}}=\overset{\text{b}}{\text{CH}}\overset{\text{a}}{\text{CH}_2}\overset{\text{i}}{\text{COOCH}_3}$	3-Z-(5-E)	3.28 (d, <i>J</i> _{ab} 7.2 Hz, 2H, H _a), 5.42–5.59 (m, 1H, H _b), 5.99 (d, <i>J</i> _{bc} 11.7 Hz, 1H, H _c), 5.35 (t, <i>J</i> _{de} 7.2 Hz, 1H, H _d), 2.02–2.09 (dt, 2H, H _e), 1.41 (pseudo sextet, 2H, H _f), 0.92 (t, <i>J</i> _{fg} 7.2 Hz, 3H, H _g), 1.73 (s, 3H, H _h), 3.69 (s, 3H, H _i)

IX	$\overset{s}{\text{C}}\text{H}_3\overset{f}{\text{C}}\text{H}_2\overset{e}{\text{C}}\text{H}=\overset{d}{\text{C}}(\overset{h}{\text{C}}\text{H}_3)\overset{c}{\text{C}}\text{H}=\overset{b}{\text{C}}\overset{a}{\text{C}}\text{HCOOCH}_3$	3-E-(5-E)	3.10 (d, J_{ab} 7.2 Hz, 2H, H_a), 5.58 (dt, J_{bc} 15.6 Hz, J_{ab} 7.2 Hz, 1H, H_b), 6.11 (d, J_{bc} 11.6 Hz, 1H, H_c), 5.41 (t, J_{de} 6.5 Hz, 1H, H_d), 2.07–2.10 (m, 2H, H_e), 1.39 (pseudo sextet, 2H, H_f), 0.90 (t, J_{fg} 7.3 Hz, 3H, H_g), 1.73 (s, 3H, H_h), 3.68 (s, 3H, H_i)
IXa	$\overset{c}{\text{C}}\text{H}_3\overset{d}{\text{C}}\text{H}_2\overset{b}{\text{C}}\text{H}=\overset{g}{\text{C}}(\overset{f}{\text{C}}\text{H}_3)\overset{e}{\text{C}}(\text{C}=\overset{h}{\text{C}}\text{H}_2)\overset{a}{\text{C}}\text{H}_2\text{COOCH}_3$	3-Z-(6-E) 3-E-(6-E)	3.30 (s, 2H, H_a), 5.56 (t, J_{bc} 7.3 Hz, 1H, H_b), 2.11 (q, J_{bc} 7.3 Hz, J_{cd} 7.3 Hz, 2H, H_d), 1.41 (sextet, J_{de} 7.3 Hz, 2H, H_e), 0.90 (t, J_{de} 7.3 Hz, 3H, H_g), 5.00 and 5.20 (s, 2H, H_f), 1.81 (s, 3H, H_g), 3.67 (s, 3H, H_h)
X	$\overset{f}{\text{C}}\text{H}_3(\overset{c}{\text{C}}\text{H}_2)_4\overset{d}{\text{C}}\text{H}_2\overset{b}{\text{C}}\text{H}=\overset{e}{\text{C}}\text{HCH}_2\text{CH}=\text{CHCH}_2\text{COOH}$	3-Z-(6-E)	3.15 (d, J_{ab} 5.3 Hz, 2H, H_a Z), 3.09 (d, J_{ab} 5.6 Hz, 2H, H_a E), 5.29–5.68 (m, 4H, H_b), 2.71–2.75 (m, 2H, H_c), 1.95–2.04 (m, 2H, H_d), 1.20–1.40 (m, 8H, H_e), 0.88 (t, J_{ef} 6.7 Hz, 3H, H_f)
XIII	$\overset{f}{\text{C}}\text{H}_3\overset{c}{\text{C}}\text{H}_2\overset{d}{\text{C}}\text{H}=\overset{e}{\text{C}}\text{HCH}_2\text{CH}=\overset{b}{\text{C}}\overset{a}{\text{C}}\text{HCOOCH}_3$	3-Z-(6-E) 3-E-(6-E)	3.15 (d, J_{ab} 6.2 Hz, 2H, H_a Z), 3.07 (d, J_{ab} 4.7 Hz, 2H, H_a E), 5.61–5.75 (m, 2H, H_b), 2.91–3.03 (m, 2H, H_c), 6.14–6.23 (m, 1H, H_d), 6.39 (d, J_{de} 15.8 Hz, 1H, H_e), 7.13–7.40 (m, 5H, H_f), 3.68 (s, 3H, H_g)
XIV	$\overset{c}{\text{C}}\text{H}_3\overset{d}{\text{C}}\text{H}=\overset{f}{\text{C}}(\overset{e}{\text{C}}\text{H}_3)\overset{b}{\text{C}}\text{H}=\overset{a}{\text{C}}\text{HCH}_2\text{COOCH}_3$	3-Z	3.35 (dd, J_{ab} 7.4 Hz, J_{ac} 1.6 Hz, 2H, H_a), 5.63 (dt, J_{bc} 11.7 Hz, J_{ab} 7.4 Hz, 1H, H_b), 6.12 (d, J_{bc} 11.7 Hz, 1H, H_c), 6.40 (s, 1H, H_d), 7.13–7.40 (m, 5H, H_e), 2.00 (d, J_{df} 1.0 Hz, 3H, H_f), 3.69 (s, 3H, H_g)
XIV	$\overset{e}{\text{C}}\text{H}_3\overset{d}{\text{C}}\text{H}=\overset{f}{\text{C}}(\overset{c}{\text{C}}\text{H}_3)\overset{b}{\text{C}}\text{H}=\overset{a}{\text{C}}\text{HCH}_2\text{COOCH}_3$	3-E	3.19 (dd, J_{ab} 7.2 Hz, J_{ac} 1.1 Hz, 2H, H_a), 5.84 (dt, J_{bc} 15.0 Hz, J_{ab} 7.2 Hz, 1H, H_b), 6.32 (d, J_{bc} 15.0 Hz, 1H, H_c), 6.46 (s, 1H, H_d), 7.15–7.40 (m, 5H, H_e), 2.00 (s, 3H, H_f), 3.71 (s, 3H, H_g)
XVI	$(\overset{d}{\text{C}}\text{H}_3)_2\overset{c}{\text{C}}=\overset{b}{\text{C}}(\overset{a}{\text{C}}\text{H}_3)\overset{e}{\text{C}}\text{H}=\overset{f}{\text{C}}\text{HCH}_2\text{COOCH}_3$	3-E	3.13 (d, J_{ab} 7.2 Hz, 2H, H_a), 5.59 (dt, J_{bc} 15.5 Hz, J_{ab} 7.2 Hz, 1H, H_b), 6.55 (d, J_{bc} 15.5 Hz, 1H, H_c), 1.76, 1.78, 1.80 (s, 9H, H_d), 3.68 (s, 3H, H_e)
XVII	$\overset{d}{\text{C}}\text{H}_3\overset{c}{\text{C}}\text{H}=\overset{b}{\text{C}}\text{HCH}(\overset{e}{\text{C}}\text{H}_3)\overset{f}{\text{C}}\text{H}=\overset{a}{\text{C}}\text{HCH}_2\text{COOCH}_3$	3-Z-(6-E)	3.07–3.12 (m, 2H, H_a), 5.32–5.49 (m, 4H, H_b), 3.00–3.05 (m, 1H, H_c), 1.64 (d, J_{bd} 4.9 Hz, 3H, H_d), 1.04 (d, J_{ce} 6.7 Hz, 3H, H_e), 3.68 (s, 3H, H_f)
XVII	$\overset{d}{\text{C}}\text{H}_3\overset{c}{\text{C}}\text{H}=\overset{b}{\text{C}}\text{HCH}(\overset{e}{\text{C}}\text{H}_3)\overset{f}{\text{C}}\text{H}=\overset{a}{\text{C}}\text{HCH}_2\text{COOCH}_3$	3-E-(6-E)	3.03 (d, J_{ab} 5.0 Hz, 2H, H_a), 5.34–5.55 (2m, 4H, H_b), 2.81–2.94 (s broad, 1H, H_c), 1.74 (d, J_{bd} 4.0 Hz, 3H, H_d), 1.15 (d, J 6.9 Hz, 3H, H_e), 3.71 (s, 3H, H_f)
XVIII	$\overset{e}{\text{C}}\text{H}_3\overset{d}{\text{C}}\text{H}=\overset{f}{\text{C}}(\overset{g}{\text{C}}\text{H}_3)\overset{b}{\text{C}}\text{H}=\overset{a}{\text{C}}\text{HCH}_2\text{COOCH}_3$	3-E-(5-E)	3.11 (d, J_{ab} 7.2 Hz, 2H, H_a), 5.63 (dt, J_{bc} 15.7 Hz, J_{ab} 7.2 Hz, 1H, H_b), 6.00 (d, J_{bc} 15.7 Hz, 1H, H_c), 5.44 (m, 1H, H_d), 1.71 (d, J_{de} 7.0 Hz, 3H, H_e), 2.24 (q, J_{fg} 7.3 Hz, 2H, H_f), 1.0 (t, J_{gh} 7.3 Hz, 3H, H_g), 3.69 (s, 3H, H_h)
XVIII	$\overset{e}{\text{C}}\text{H}_3\overset{d}{\text{C}}\text{H}=\overset{f}{\text{C}}(\overset{g}{\text{C}}\text{H}_3)\overset{b}{\text{C}}\text{H}=\overset{a}{\text{C}}\text{HCH}_2\text{COOCH}_3$	3-E-(5-Z)	3.17 (d, J_{ab} 7.2 Hz, 2H, H_a), 5.76 (dt, J_{bc} 15.7 Hz, J_{ab} 7.2 Hz, 1H, H_b), 6.45 (d, J_{bc} 15.7 Hz, 1H, H_c), 5.41 (m, 1H, H_d), 1.72 (d, J_{de} 6.9 Hz, 3H, H_e), 2.19 (q, J_{fg} 7.3 Hz, 2H, H_f), 1.05 (t, J_{gh} 7.3 Hz, 3H, H_g), 3.70 (s, 3H, H_h)

^a All assignments based on indirect evidence (see text) are placed in brackets. The stereochemistry of the trisubstituted 5-double bond of IXa and XIV was not determined.

1,3-pentadiene and 1,2-pentadiene; the ratio of linear to branched product is 23/77 in the former case and 59/41 in the latter. The ratio is increased when bulkier groups are attached to the allene systems, and reaches 73/27 with 1,2-hexadiene and 90/10 with phenylallene.

The ratio of linear to branched product can be substantially varied by appropriate choice of ligands, and very low ratios (as low as 5/95) can be attained both with phosphites and with tributylphosphine. In the present stage of knowledge we cannot account for of this.

A curious aspect of the reaction with phosphites as ligands is the presence of small amounts of acids resulting from attack on the internal position of the 3-butenic double bond. These compounds are not present with triphenylphosphine.

It is noteworthy that no 3,5-acids, which could come from the vinyl group $\text{RCH}_2\text{C}=\text{CH}_2$ (Scheme 1, formula in parentheses) which might be formed by hydride attack on the allenes, were found, possibly because their reaction products with 3-butenic acid isomerize to the same compounds as were formed from the isomeric vinyl species.

It is evident that the reaction described allows ready access to compounds not easily obtainable by other ways, and offers efficient control of the regioselectivity.

Experimental

The starting materials 1,2-propadiene [6], 1,2-pentadiene [7], 1,2-hexadiene [8], 1,2-nonadiene [9], 1-phenyl-1,2-propadiene [10], 3-methyl-1,2-butadiene [11] and 2,3-pentadiene [12] were prepared by published procedures.

The starting complexes were obtained from Strem. The products were analyzed by GLC on a capillary SE 52 (silicone) column with internal standard and separated on a UCC 982 (10% silicone on chromosorb) column. The elution order of the isomers was generally: branched 3,6 (3-Z-6-E and 3-E-6-E), 3,5 (3-Z), linear 3,6 (3-Z-6-E and 3-E-6-E), 3,5 (3-E).

Mass spectra were recorded with a Varian CH5 instrument (70 eV). ^1H NMR spectra were recorded on Varian XL-100 and Bruker WM 300 instruments.

General procedure

The catalyst, 3-butenic acid, and the allene in 1:70–850:50–800 molar ratio were placed in a glass container able to withstand a pressure of a few atmospheres and heated in an oil bath at 85°C with magnetic stirring. The mixture obtained was separated by conventional acid–base treatment.

Table 4 lists NMR data for new compounds.

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