# Co-oligomerization of Butadiene and Carbon Dioxide Catalysed by Tertiary Phosphine–Palladium Complexes

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Tertiary phosphine–palladium complexes catalyse the co-oligomerization reaction of butadiene and carbon dioxide under mild conditions of temperature and pressure (70 °C, 100 atm) to yield (E)-2-ethylidenehept-6-en-5-olide (2) and octadienyl esters of (E)-2-ethylidenehepta-4,6-dienoic acid (3b, c) and of 2-vinylhepta-4,6-dienoic acid (4b, c). At higher temperature (90 °C) esters (3b, c) yield octa-1,3,7-triene and (E)-2-ethylidenehepta-4,6-dienoic acid through an oxidative addition of the allyl carbon–oxygen bond to a palladium(o) species. Subsequent reactions of the carboxylic acid in the presence of $[PdL_n]$ (L = tertiary phosphine) complexes yield (E)-2-ethylidenehept-5-en-4-olide (1) and 2-ethylhepta-2,4-dien-4-olide (5).

THERE is currently considerable interest in the fixation of carbon dioxide to organic substrates using transition-metal catalysts. This interest has been fostered by recent reports on the isolation and structural characterization of CO_2–metal complexes [1] as well as the insertion of CO_2 into the transition-metal–carbon bond.[2] A few examples of co-oligomerization reactions of butadiene [3,4] and acetylenic compounds [5] with CO_2 have been recently reported.

It has been previously shown that CO_2 at low pressures
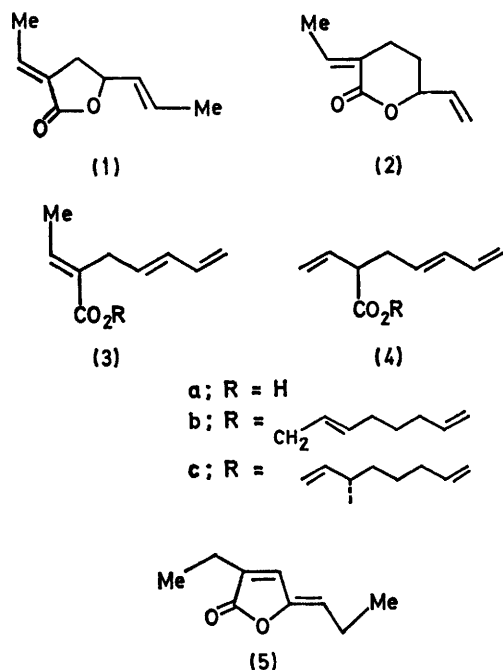
greatly enhances the catalytic properties of platinum- and palladium–phosphine complexes in the dimerization reactions of butadiene and isoprene.[6-8] It has also been found that CO_2 acts as a co-catalyst with palladium complexes in the reaction of butadiene and water to yield octadienols.[9] Subsequently Inoue and co-workers have found that $[Pd(diphos)_2]$ (diphos = $Ph_2PCH_2CH_2$-PPh_2) catalyses the telomerization reaction of butadiene and CO_2 at 120 °C in polar and aprotic solvents to give the γ-lactone 2-ethylidenehept-5-en-4-olide (1) in small yields.[3] Surprisingly $[Pd(PPh_3)_4]$ was found to be even

less active in this reaction. Here we report that palladium complexes of unidentate tertiary phosphine ligands, PPh_3 among them, catalyse the co-oligomerization of butadiene and CO_2 in non-polar solvents (e.g. benzene) to yield a δ-lactone, (E)-2-ethylidenehept-6-en-5-olide (2), and the octadienyl esters of (E)-2-ethylidene-hepta-4,6-dienoic acid (3b, c) and 2-vinylhepta-4,6-dienoic acid (4b, c).† Lactone (1) as well as its isomer, 2-ethylhepta-2,4-dien-4-olide (5), are obtained by further reaction of (3a) in the presence of $[PdL_n]$ (L = tertiary phosphine) complexes.

RESULTS

We have recently reported that $[PdL_n]$ complexes in the presence of CO_2, at low pressures (5—10 atm ‡) and 110 °C, are effective catalysts for the dimerization of butadiene to octa-1,3,7-triene, which is subsequently isomerized to octa-2,4,6-triene.[7] In the absence of CO_2 the butadiene conversion to dimer is very low, therefore it may be concluded that, in the reaction conditions given above, CO_2 behaves as a co-catalyst in the dimerization reaction. However at substantially higher CO_2 pressure and lower temperature (80—100 atm, 70 °C), CO_2 becomes a reagent and butadiene–CO_2 co-oligomers (2)—(4) are formed in addition to butadiene dimers. The reaction of CO_2 with butadiene is catalysed by pre-formed palladium(0)–phosphine complexes, but more conveniently the catalyst may be prepared in situ by mixing $[\{\eta^3\text{-}2\text{-methylallyl})\text{PdOAc}\}_2]$ with the appropriate phosphorus ligand in the chosen Pd : L ratio. In the cases of L = $P(C_6H_{11})_3$, PBu^t_2Ph, and PEt_3 the catalytic reaction was performed both using PdL_n and $[\{\eta^3\text{-}2\text{-methylallyl})PdOAc\}_2]$: L as the catalyst the Pd : L ratio being kept constant. No significant difference was found in the product distribution for the two catalysts. Consequently all subsequent work has been performed using the $[\{\eta^3\text{-}2\text{-methylallyl})PdOAc\}_2]$: L system.

As shown in the Table the distribution of the reaction products depends on the ligand bound to palladium. $P(C_6H_{11})_3$ and PPr^i_3 gave the best yields on the δ-lactone (2). With $P(C_6H_{11})_3$ as the ligand the presence of catalytic quantities of water appeared necessary in order to have reproducible results. When using either $[Pd\{P(C_6H_{11})_3\}_2]$ or a mixture of $[(C_4H_7PdOAc)_2]$ and $P(C_6H_{11})_3$ as the catalyst the telomerization reaction in the absence of water often proceeded at very low conversions, due to the separ-

† These results have been reported in a preliminary communication.[4]

‡ 1 atm = 101.325 N m⁻².

ation of the palladium catalyst as an insoluble pale yellow solid; the low solubility of this complex prevented structural elucidation by n.m.r. spectroscopy. The elemental analysis is consistent for $[Pd(C_4H_6)_2\{\overset{\cdot}{P}(C_6H_{11})_3\}(CO_2)]$. The i.r. spectrum (Nujol mull) displays a strong absorption at 1 610 cm^{-1}, which compares with that found recently for some allyl–Ni–carboxylate compounds.[29] The presence of small quantities of water prevent the catalyst from separating out, and allowing the reaction to proceed. As expected minute quantities of octadienols are also formed by reaction of water and butadiene.[9] Esters (3b, c) and (4b, c) are the major reaction products in the

for a few hours at 90 °C. In this thermal treatment, degradation of esters (3b, c) to octa-1,3,7-triene and the carboxylic acid (3a) also occurs. For example, on heating the reaction products obtained using Pd–PEt$_3$ after elimination of the volatile components (i.e. solvent and octa-1,3,7-triene) for 6 h at 90 °C, 35% of the co-oligomerization products are decomposed to carboxylic acid (3a) and octa-1,3,7-triene. The carboxylic acid (3a) is a 2 : 1 mixture of the trans and cis isomer on the 4,5-double bond, which is clearly shown by the ^{1}H n.m.r. spectrum recorded at 270 MHz.

As pointed out by Inoue and co-workers, the carboxylic

TABLE

Butadiene and carbon dioxide co-oligomerization catalysed by tertiary phosphine–palladium complexes [a]

| Ligand | $\overset{3}{\underset{i=1}{\Sigma}} X_i$[b]/cm^{-1} | ν [c]/° | Product yield (%) [d] | | | |
			1,3,7-OT [e]	Esters [f]	(2)	Others [g]
P(C$_6$H$_{11}$)$_3$ [h]	0.3	170	14	14	28	6
PPr$^i_3$	3.1	160	25	19	27	7
PBu$^t_2$Ph [h]	4.3	170	10	1	1	
PEt$_3$	5.6	132	44	29		12
PMe$_2$Ph	9.2	122	41	46		8
P(CH$_2$Ph)$_3$	10.3	165	14	44	5	17
P(o-tolyl)$_3$	10.5	194	60	8		
PMePh$_2$	10.9	136	66	27		14
PPh$_3$ [h]	12.8	145	11	17	3	34

[a] Butadiene 0.31 mol, $[\{(\eta^3\text{-}2\text{-methylallyl})PdOAc\}_2]$ 0.38 mmol, ligand 2.28 mmol, CO$_2$ 0.59—0.60 mol; 80 ml autoclave; 70 °C, 20 h [40 h for the P(C$_6$H$_{11}$)$_3$ run]. [b] Ligand electronic parameter, $\nu_{CO(A_1)}$ $[Ni(CO)_3L] = \overset{3}{\underset{i=1}{\Sigma}} X_i + 2\,056.1$ cm^{-1} (ref. 13). [c] Ligand cone angle (ref. 13). [d] The yields are based on butadiene conversion. [e] OT = Octatriene. [f] Mixtures of esters (3b, c) and (4b, c) except for the PBu$^t_2$Ph and P(o-tolyl)$_3$ reactions where esters (4b c) are formed. [g] Uncharacterized butadiene–CO$_2$ telomers and small quantities of acids (3a) and (4a); percentage in weight referred to the overall amount of telomers formed in the reaction. [h]H$_2$O (3.9 mmol) was present in the reaction mixture.

presence of PMe$_2$Ph, PMePh$_2$, PEt$_3$, PPh$_3$, P(CH$_2$Ph)$_3$, and P(o-tolyl)$_3$. Small quantities of the δ-lactone (2) are formed in the presence of PPh$_3$ and P(CH$_2$Ph)$_3$ as ligands. In the PPh$_3$ catalytic runs it was found that the presence of small quantities of water in the reaction medium significantly increases the butadiene conversion to butadiene–CO$_2$ co-oligomers. In the absence of water the butadiene conversion (with respect to PPh$_3$ in the Table) is reduced by as much as 50%. In some aspects this behaviour parallels that observed for P(C$_6$H$_{11}$)$_3$. On raising the PPh$_3$: Pd ratio from 3 : 1 to 4 : 1 the butadiene conversion to esters drops from 17 to 8%, whereas butadiene conversion to lactone (2) rises from 3 to 7%. However, at this high PPh$_3$: Pd ratio part of the Pd catalyst separates out from the reaction mixture as $[Pd(PPh_3)_n]$. The ratio in which (3b, c) and (4b, c) are formed depends on the phosphorus ligand co-ordinated to the metal. Esters (3b, c) are mainly formed (80%, b/c ∼ 2) with all the ligands indicated in the Table except P(o-tolyl)$_3$, PBu$^t_2$Ph, and PPh$_3$. In the presence of PPh$_3$ the esters (3b, c) and (4b, c) are formed in comparable amounts whereas esters (4b, c) are preferentially formed with P(o-tolyl)$_3$ and PBu$^t_2$Ph. The latter tertiary phosphines gave very low conversions of butadiene to CO$_2$ telomers. This is very probably due to the large size of the ligand which deactivates the catalytic species. However in the PBu$^t_2$Ph reaction, esters (4b, c) and lactone (2) are obtained in comparable quantities while P(o-tolyl)$_3$ gives the esters (4b, c) as the major products.

The esters (4b, c) are the precursors of the esters (3b, c). In the catalytic runs where mixtures of esters are present, esters (4b, c) are isomerized to esters (3b, c) by heating the crude reaction products, which still contain the catalyst,

acid (3a) is the precursor of the γ-lactone (1). By heating (3a) for 7 h at 90 °C in the presence of $[Pd(PEt_3)_3]$ as the catalyst, (1) is obtained (39% yield). At longer reaction times (20 h), (1) is isomerized to (5) which can be isolated in low yields (12%). Better yields of (5) (42%) are obtained by heating (3a) in the presence of $[Pd\{P(C_6H_{11})_3\}_2]$ for shorter times (6 h).

The ethylidene side-chains of (1)—(3) have the E stereochemistry as demonstrated by ^{13}C n.m.r. spectroscopy. The $^3J_{C-H}$ value (ca. 5 Hz) of the carbon of the carbonyl group and the ethylidene proton compares for compounds (1)—(3) with the value (6.78 Hz) found in crotonic acid, and is smaller than that found in isocrotonic acid (14.50 Hz).[10]

The lactone (1) has a trans geometry at the 5,6-double bond according to the i.r. spectrum (970 cm^{-1}) and the $J_{H-5-H-6}$ coupling constant (15 Hz).

Lactone (5) has been prepared as a mixture of E- and Z-isomers; however, by silica gel chromatography, one isomer (which is eluted first) has been obtained pure. Comparison of the ^{1}H n.m.r. spectrum of the pure product with that of the mixture has permitted the assignment of a Z-stereochemistry to it. The assignment is based on the assumption, widely tested in γ-alkylidene-$\Delta^{\alpha,\beta}$-butenolides, that the olefinic proton trans to the lactone oxygen resonates at higher field (δ 5.15) than that of the cis analogue (δ 5.64).[11]

The structure of esters (3b, c), which could not be separated by column chromatography, is based on the ^{1}H n.m.r. spectrum and on the identification of the saponification products of the mixture [i.e. (3a), octa-2,7-dien-1-ol and octa-1,7-dien-3-ol]. The ^{1}H n.m.r. spectrum at 270

MHz, although complex, allows assignment of the resonances by spin-decoupling experiments. Analogously, the structure of esters (4b, c) is based on the high-field [1]H n.m.r. spectrum. Saponification of esters (4b, c) yielded
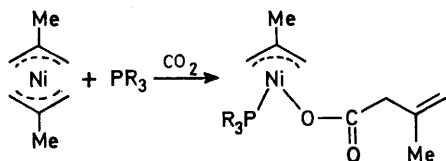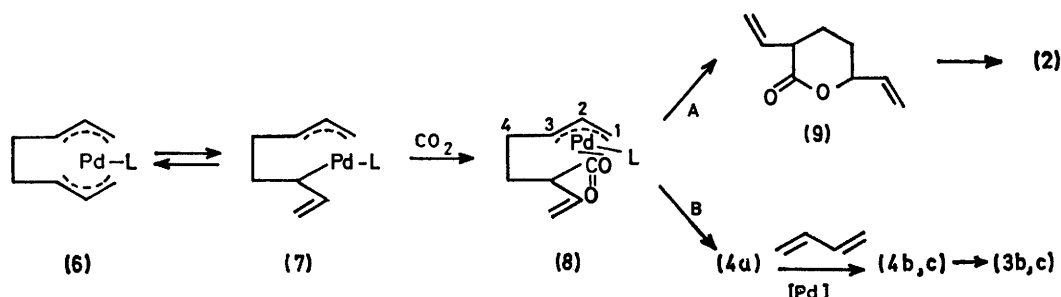

SCHEME 1

octadienols and the acid (3a) due to isomerization of esters (4b, c) to (3b, c) in alkaline medium.

DISCUSSION

Wilke and his co-workers [2g] have recently reported reactions of CO_2 with allyl–Ni complexes. For example, in the presence of tertiary phosphine ligands [Ni-(η^3-2-methylallyl)$_2$] reacts with CO_2 to yield a carboxylate species (see Scheme 1). This reaction has been interpreted as an insertion of CO_2 into the σ-allyl–Ni bond promoted by the tertiary phosphine ligand. A similar insertion reaction is probably involved in the

proposed by Inoue and co-workers,[3] involves a hydrogen shift from C-4 to oxygen. The intermediate lactone (9) is formed by nucleophilic attack of oxygen to C-3. Lactone (9), which we have not isolated, is isomerized in the reaction medium to lactone (2). The octadienyl esters (4b, c) are formed by further reaction of the acid with butadiene. It is known that organic compounds with active hydrogens in the presence of palladium complexes give 1-substituted octa-2,7-dienes together with 3-substituted octa-1,7-dienes.[12] As shown in Table 1 the preferential formation of esters or δ-lactones depends on the phosphorus ligand bound to the metal. The results obtained with PPr$^i_3$ and P(C$_6$H$_{11}$)$_3$ compared with those obtained with smaller cone-angle ligands [13] (e.g. PEt$_3$, PMe$_2$Ph, etc.) suggest prima facie that the bulkier the tertiary phosphine the larger the percentages of δ-lactone formed. However the product distribution obtained with the bulkier PBu$^t_2$Ph and P(o-tolyl)$_3$, although these ligands give the lowest conversions of butadiene to telomers, does not support this view. Comparison of the electronic character $\sum_i \chi_i$ of the ligands, introduced by Tolman,[13] with product distribution suggests that the δ-lactone is preferentially

SCHEME 2
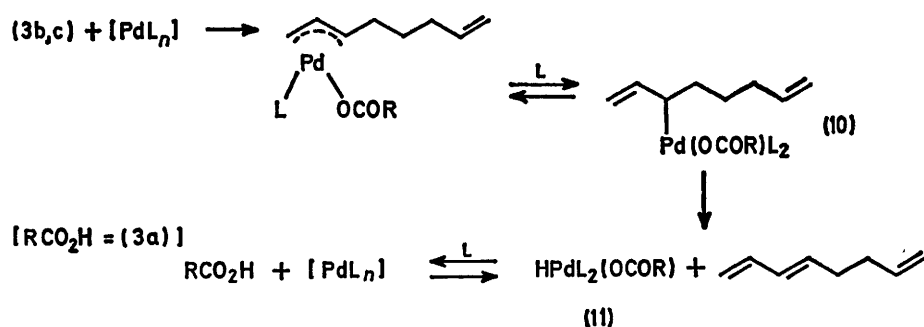
SCHEME 3

co-oligomerization reaction of butadiene and CO_2 catalyzed by tertiary phosphine–palladium complexes as indicated in the Scheme 2. Species (6) and (7) are generally accepted as intermediates in the palladium-catalysed linear dimerization of butadiene.[12] The insertion of CO_2 into the σ-allyl bond of (7) gives the carboxylate intermediate (8) which may react either via route A to give the lactone (9) or via route B to give the carboxylic acid (4a). The formation of the acid (4a), as

formed with the more basic phosphines [i.e. P(C$_6$H$_{11}$)$_3$, PPr$^i_3$]. Esters are principally formed with ligands less basic than PBu$^t_2$Ph. A slight deviation from this trend is however observed for PPh$_3$ and P(CH$_2$Ph)$_3$, since small quantities of δ-lactone are formed with these ligands.*

* Recently Heimbach and co-workers have reported an elegant example of electronic control of the phosphorus ligand in the co-oligomerization reaction of butadiene with acetophenone and morpholine.[14]

Esters (4b, c) are the precursors of esters (3b, c) since they are isomerized to the latter on heating, at 90 °C, the crude reaction mixture, which still contains the catalyst. The isomerization reaction is probably catalysed by a Pd–H species present in the reaction mixture. No isomerization was observed on heating mixtures of (3b, c) and (4b, c) in the presence of free PEt_3. The thermal treatment of the crude reaction mixture in the presence of the palladium catalyst also

et al.[17] [$Pd(PEt_3)_3$], [$Pd\{P(C_6H_{11})_3\}_2$], and [$Pd(PBu^t_2Ph)_2$] were prepared according to published procedures.[18] [$\{(\eta^3\text{-}2\text{-}$Methylallyl)PdOAc\}_2$] was prepared with a slight modification of the method reported by Robinson and Shaw,[19] by treating the corresponding chloro-complex with TlOAc in THF.

[1]H N.m.r. spectra were recorded at 270 MHz on a Bruker HX instrument and a Bruker HFX 90 spectrometer was used for [13]C n.m.r. measurements at 22.6 MHz. G.l.c. analyses were performed on a C. Erba Fractovap 2101
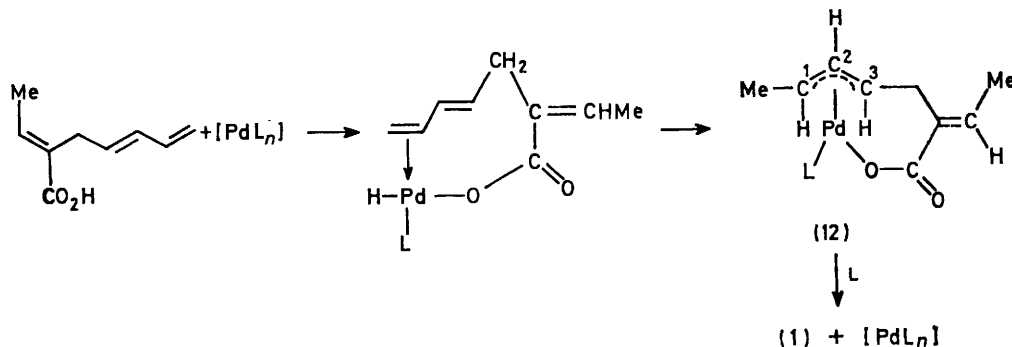
SCHEME 4

produces degradation of the octadienyl esters to the carboxylic acid (3a) and octa-1,3,7-triene. This result may be explained as an oxidative addition of the allyl carbon–oxygen bond to a palladium(0) species (Scheme 3). Elimination of octa-1,3,7-triene from (10) gives the Pd–H species (11) which is in equilibrium with the carboxylic acid (3a) and the [PdL_n] complex. The proposed reaction scheme has a precedent in the degradation reaction reported by Smutny of 1-phenoxyocta-2,7-diene to octa-1,3,7-triene and phenol, catalysed by [$Pd(PPh_3)_n$].[15] Moreover Tsuji and co-workers have recently reported the formation of conjugated dienes on elimination of acetic acid and phenol from allylic acetates and allylic phenyl ethers, respectively, in the presence of [$Pd(PPh_3)_n$].[16]

Carboxylic acid (3a) is easily converted to the γ-lactone (1) by [PdL_n] complexes. The mechanism indicated in Scheme 4 may be proposed for this reaction. Lactone (1) may be formed through nucleophilic attack of oxygen to C-3 of the intermediate complex (12). Lactone (1) is isomerized to lactone (5) at long reaction times.

Conclusions.—The present work shows that unidentate tertiary phosphine–palladium(0) complexes are effective catalysts for the telomerization reaction of butadiene and CO_2. The reaction may be carried out at moderately low temperature and pressure in non-polar solvents. The key step of the reaction is thought to be the insertion of CO_2 into a σ-allyl–Pd bond promoted by the ligand. The distribution of the products formed is controlled to some extent by the choice of ligand.

EXPERIMENTAL

Butadiene (Phillips, rubber grade) was distilled over molecular sieves. CO_2 (Siad, Milan) was 99.9% pure. All the tertiary phosphines were commercially obtained (Strem) except PBu^t_2Ph which was prepared according to Mann

instrument [1% D-Lac 769 on Chromosorb WHF, 3 m × 6 mm glass column, N_2 as the carrier gas, temperature: 170 °C for esters (3) and (4), 130 °C for (1), (2), and (5)].

Procedure for Catalytic Runs.—All the operations were carried out under a nitrogen atmosphere. To a benzene solution (10 ml) of [$\{C_4H_7PdOAc\}_2$] (0.168 g, 0.38 mmol) was added the appropriate ligand (2.28 mmol). The catalyst solution was siphoned onto butadiene (17 g, 0.31 mol) at −20 °C. The resultant solution was siphoned into an 80-ml high-pressure stainless-steel autoclave, previously cooled and evacuated, which contained a Teflon-coated bar for magnetic stirring and water (70 mg, 3.9 mmol) if necessary [$P(C_6H_{11})_3$, PPh_3, and $P(o\text{-tolyl})_3$ runs]. Carbon dioxide was then introduced. The weight of CO_2 (26—27 g, 0.59—0.60 mol) was controlled by weighing the autoclave with a balance accurate to ±1 g. The autoclave was occasionally cooled below room temperature to introduce the desired amount of CO_2. The autoclave was then placed in an oil-bath at 70 °C for 20 h. A longer reaction time (40 h) was found convenient for the $P(C_6H_{11})_3$ run. The pressure reached in the reaction vessel was 80—100 atm. **CAUTION**: introduction of larger quantities of CO_2 produced much higher pressures owing to the small volume of the autoclave. Pressures higher than 100 atm are not advisable as they do not significantly affect the telomer yields.

Separation of the Reaction Products.—The excess of CO_2 and unchanged butadiene was vented at room temperature and then the reaction mixture was flash-distilled (10⁻³ mmHg, 20 °C) to eliminate the volatile components (benzene and octa-1,3,7-triene). A small portion (1—2 g) of the oily residue was extracted with aqueous NaOH (1%) to eliminate small quantities of carboxylic acids (3a) and (4a) present in the reaction mixture, and then passed through a silica gel column (20 × 2.5 cm) eluting with cyclohexane–ethyl acetate (50 : 1—5 : 1). This procedure was found convenient to eliminate the catalyst and simplify the g.l.c. analysis. Mixtures of esters (3b, c) and (4b, c) are eluted first and then the δ-lactone (2). The yields reported in the

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Table are referred to the weights of column chromatography fractions; therefore they should be considered approximate. Generally between the ester and lactone fractions small quantities of a viscous oil were eluted, with an i.r. spectrum similar in many aspects to those of esters (3) and (4). This material was not obtained pure and was not further investigated (unidentified products in the Table).

(E)-2-*Ethylidenehept-6-en-5-olide* (2).—A part (1.7 g) of the reaction product (12 g) obtained in the PPr$^i_3$ catalytic run, after removal *in vacuo* of solvent and octa-1,3,7-triene, was diluted with ether and extracted with aqueous NaOH (1%) to eliminate small quantities of carboxylic acids (3a) and (4a) (0.08 g). Evaporation of the ethereal phase after drying (CaSO$_4$) gave a yellow oil (1.6 g). Chromatography on a silica gel column (20 × 2.5 cm) eluting with cyclohexane–ethyl acetate (50 : 1—5 : 1) gave esters (3b, c) and (4b, c) [0.5 g, (3) : (4) = 4 : 1], followed by minute quantities of unidentified products (0.03—0.04 g), and then the lactone (2) (0.9 g). Comparable results were obtained by column chromatography of the P(C$_6$H$_{11}$)$_3$ reaction products. Lactone (2) (Found: C, 71.35; H, 8.05. Calc. for C$_9$H$_{12}$O$_2$: C, 71.03; H, 7.95%); ν$_{max.}$ (neat) 1 710 cm^{-1} (C=O); δ(CDCl$_3$) 1.79 (d, J 7.5 Hz, Me), 1.79—2.08 (m, CH$_2$CH), 2.46—2.60 (m, =CCH$_2$), 4.78 (m, CH$_2$CH), 5.21 (d, J 10.7 Hz, CH=CH$_2$, 1 H, *cis* H), 5.34 (d, J 17.2 Hz, CH=CH$_2$, 1 H, *trans* H), 5.89 (m, CH=CH$_2$), and 7.07 (m, MeCH=); ^{13}C{^{1}H} n.m.r. (CDCl$_3$), δ 164.93 (C=O), 139.66 (MeCH=), 135.19 (CH=CH$_2$), 125.37 (=C<), 115.56 (=CH$_2$), 77.88 (−CH<), 26.70 (−CH$_2$CH<), 21.02 (=CCH$_2$−), and 13.06 (Me); the assignment was made by selective proton decoupling.

2-*Vinylhepta-4,6-dienoic Acid* (4a).—This acid can be obtained only in small quantities. Aqueous NaOH (1%) extraction of the reaction products obtained with P(o-tolyl)$_3$ afforded 0.06—0.08 g of (4a). Alkaline extraction of butadiene–CO$_2$ telomers obtained as in the Table with other ligands yielded small amounts of mixtures of the acids (3a) and (4b); e.g. aqueous NaHCO$_3$ extraction of the reaction products obtained with PPh$_3$ as the ligand afforded 0.4 g of acids. Silica gel chromatography (cyclohexane–ethyl acetate) of a portion of this mixture (0.1 g) yielded (4a) (0.04 g), eluted first, and then the acid (3a) (0.03 g). Acid (4a): ν$_{max.}$ (neat) 1 705 cm^{-1} (C=O); δ(CDCl$_3$) 2.58—2.40 (m, CH$_2$), 3.13 (m, CH), 5.02, 5.13, 5.20, and 5.21 (doublets, J ~ 10, 15, 10, and 15 Hz, respectively, =CH$_2$), 5.66 (m, CH$_2$CH=), 5.86 (m, CHCH=), 6.11 [dd, J 15 (*trans* double bond) and 10 Hz, −CH=CH−CH=], and 6.31 (m, =CHCH= CH$_2$); low intensity signals at δ 2.68, 5.37, and 6.60 are attributable to the *cis* isomer.

Octadienyl Esters of 2-Vinylhepta-4,6-dienoic Acid (4b, c). —The reaction product obtained with PBu$^t_2$Ph as the ligand (1.22 g) was passed through a silica gel column eluting with cyclohexane–ethyl acetate as described above for the lactone (2). Esters (4b, c) were eluted first (0.24 g, b : c ~ 2 : 1) and then, in the order, unidentified butadiene–CO$_2$ telomers (0.06 g) and the lactone (2) (0.21 g). Esters (4b, c); ν$_{max.}$ (neat) 1 730 cm^{-1} (C=O); δ(CDCl$_3$) C$_8$H$_{11}$CO$_2$ fragment 2.48—2.37 (CH$_2$), 3.11 (CH), 4.93—5.25 (=CH$_2$), 5.60 (CH$_2$CH=), 5.77 (=CHCH), 6.08 (−CH=CHCH=), and 6.28 (=CHCH=CH$_2$); C$_8$H$_{13}$ fragment 1.48 [CH$_2$CH$_2$CH$_2$ (4b, c)], 1.62 [CHCH$_2$CH$_2$, (4c)], 2.06 [CH$_2$CH=, (4b c)], 4.55 [OCH$_2$, (4b)], 4.93—5.28 [=CH$_2$, (4b, c) and CH, (4c)], 5.60 [OCH$_2$CH=, (4b)], and 5.77 [CH=CH$_2$, (4b) and OCH$_2$CH=CH, (4b)].

(E)-2-*Ethylidenehepta-4,6-dienoic Acid* (3a) *and the Octa-*

dienyl Esters (3b, c).—A part (5.6 g) of the crude reaction product obtained in the PEt$_3$ catalytic run (7 g, after evaporation *in vacuo* of solvent and octa-1,3,7-triene) was warmed at 90 °C for 6 h under N$_2$. The mixture, after removal *in vacuo* of the octa-1,3,7-triene formed (0.8 g), was diluted with ether and extracted with aqueous NaOH (1%). Evaporation of the ethereal phase, after drying on CaSO$_4$, gave a yellow oil. Chromatography on a silica gel column (cyclohexane–ethyl acetate, 50 : 1) gave esters (3) (2.5 g, b : c ~ 2 : 1). The NaOH extracts, upon acidification with diluted H$_2$SO$_4$ and extraction with ether gave crude (3a) (1.25 g). A pure sample (m.p. 42—43 °C) was obtained by chromatography on silica gel (cyclohexane–ethyl acetate, 5 : 1).

(3a) (Found: C, 71.3; H, 7.85. Calc. for C$_9$H$_{12}$O$_2$: C, 71.03; H, 7.95%): ν$_{max.}$ (Nujol) 1 680 cm^{-1} (C=O); δ(CDCl$_3$): *trans*-isomer, ca. 1.86 (d, J 7.5 Hz, Me), 3.11 (d, J 7.5 Hz, CH$_2$), 4.97 (d, J 10.5 Hz, CH=CH$_2$, 1 H, *cis*-H), 5.10 (d, J 16.5 Hz, CH=CH$_2$, 1 H, *trans*-H), 5.68 (dt, J 15 and 7 Hz, CH$_2$CH=), 6.02 (m, CH=CHCH=), 6.26 (m, CH=CH$_2$), and 7.08 (q, J 7.5 Hz, MeCH=); *cis*-isomer: ca. 1.86 (d, J 7.5 Hz, Me), 3.22 (d, J 7 Hz, CH$_2$), 5.14 (d, J 10.5 Hz, CH=CH$_2$, 1 H, *cis*-H), 5.20 (d, J 16.5 Hz, CH=CH$_2$, 1 H, *trans*-H), 5.33 (br q, J 7 and 10 Hz, CH$_2$CH=), 6.02 (m, CH=CHCH=), 6.75 (m, CH=CH$_2$), and 7.04 (q, 7.5 Hz, MeCH=). ^{13}C{^{1}H} N.m.r. δ (CDCl$_3$): *trans*-isomer (*cis*-isomer in square brackets) 173.1 [173.1] (CO$_2$H), 141.4 [141.0] (MeCH=), 136.8, 131.9, and 130.9 [131.9, 129.6, and 128.6] (=CH−), 130.9 and 130.4 (=C< of both isomers, not distinguishable), 115.5 [117 6] (=CH$_2$), 28.8 [24.8] (CH$_2$), and 14.4 [14.4] (Me); the assignment was assisted by off-resonance multiplicity.

(3b, c): ν$_{max.}$ (neat) 1 710 cm^{-1} (C=O); δ(CDCl$_3$): C$_8$H$_{11}$CO$_2$ fragment, same chemical shifts for both (3b) and (3c), *trans*-Δ^{4,5} (in brackets *cis*-Δ^{4,5}), 1.82 [1.82] (Me), 3.11 [3.22] (CH$_2$), 4.93—5.25 [4.93—5.25] (=CH$_2$), 5.62 [5.33] (CH$_2$CH=), 6.04 [6.04] (CH=CHCH), 6.24 [6.75] (CH=CH$_2$), 6.91 [6.91] (MeCH=); C$_8$H$_{13}$ fragments: 1.48 [CH$_2$CH$_2$CH$_2$, (3b, c)], 1.64 [CHCH$_2$, (3c)], 2.06 [CH$_2$CH=, (3b, c)], 4.56 [OCH$_2$, (3b)], 4.93—5.25 [=CH$_2$, (3b, c)], 5.33 [OCH, (3c)], 5.62 [CH=CHCH$_2$, (3b)], and 5.77 [CH=CHCH$_2$, (3b) and CH=CH$_2$, (3b, c)].

Saponification of Octadienyl Esters of (E)-2-*Ethylidene-hepta-4,6-dienoic Acid* (3b, c).—Ester (3b, c) (1 g) was added to a solution of water (6 ml), methanol (12 ml), and NaOH (1 g), and stirred for 48 h at room temperature. After concentration of the solution by evaporation *in vacuo* the residue was diluted with water (10 ml) and then extracted with ether. The ether extracts were dried (CaSO$_4$) and evaporated to yield octa-2,7-dien-1-ol and octa-1,7-dien-3-ol (0.4 g, 2 : 1 by g.l.c.), identified by the ^{1}H n.m.r. spectrum and g.l.c. comparison with authentic samples.[9] The aqueous layer, upon acidification with diluted H$_2$SO$_4$ and extraction with ether, gave acid (3a) (0.5 g).

(E)-2-*Ethylidenehept-5-en-4-olide* (1).—A benzene solution (10 ml) of acid (3a) (1.0 g, 6.6 mmol) and [Pd(PEt$_3$)$_3$] (0.070 g, 0.15 mmol) was syringed into a vial under nitrogen. The vial was sealed *in vacuo* and heated at 90 °C for 7 h. From the reaction products, after extraction of the unchanged acid with aqueous NaOH (1%), the lactone (1) (0.4 g) was obtained upon silica gel chromatography (cyclohexane–ethyl acetate, 5 : 1) (Found: C, 71.15; H, 8.2. Calc. for C$_9$H$_{12}$O$_2$: C, 71.03; H, 7.95%); ν$_{max.}$ (neat) 1 755 cm^{-1} (C=O); δ(CDCl$_3$) 1.73 (br d, J 6.5 Hz, CH=CHMe), 1.85 (br d, J 7.1 Hz, MeCH=C), 3.05—2.56 (m, CH$_2$), 4.91

(m, CH), 5.51 (dd, J 15 and 7.2 Hz, CHCH=), 5.83 (m, CH=CHMe), and 6.75 (m, MeCH=C); ^{13}C{^{1}H} n.m.r. (CDCl$_3$); δ 170.15 (C=O), 134.91 (MeCH=C), 129.60 and 129.24 (CH=CH), 126.93 (=C<), 77.38 (CH), 17.16 (CH=CHMe), and 15.20 (MeCH=C); the assignment of the resonances was assisted by selective proton decoupling.

2-*Ethylhepta*-2,4-*dien*-4-*olide* (5).—Acid (3a) (1.6 g, 10.52 mmol) was dissolved in benzene (15 ml) and then [Pd-{P(C$_6$H$_{11}$)$_3$}$_2$] (0.151 g, 0.23 mmol) was added. The benzene solution was syringed into a vial, which was sealed *in vacuo*, and then heated at 90 °C for 6 h. The reaction product, after evaporation of the solvent, was subjected to silica gel chromatography, eluting with cyclohexane–ethyl acetate (9 : 1) to give first the Z-isomer of (5) (0.152 g) and then a mixture of (Z,E)-isomers (*ca.* 4 : 1, 0.510 g). Subsequent fractions contained mixtures of isomerization products of (1) (0.261 g), which were not identified, and small quantities of (1) (0.14 g). The chromatography fractions were pale yellow due to the presence of small quantities of catalyst, which can be eliminated by high-vacuum trap-to-trap distillation. Compound (5) (Found: C, 70.85; H, 8.2. Calc. for C$_9$H$_{12}$O$_2$: C, 71.03; H, 7.95%); ν$_{max.}$ (neat) 1 760 cm^{-1} (C=O); δ(CDCl$_3$): Z-isomer (E-isomer in square brackets) 1.08 (t, J 7.5 Hz) [*ca.* 1.08] (Me), 1.20 (t, J 7.5 Hz) [*ca.* 1.20] (Me), 2.38 (m) [2.31] (CH$_2$), 5.15 (t, J 7.5 Hz) [5.64] (=CHCH$_2$), and 6.97 (br s) [7.26] (C=CH).

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