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Syngas Reactions

I. The Catalytic Carbonylation of Conjugated Dienes

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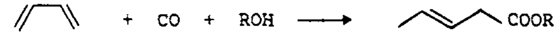
3,8-Nonadienoate acid esters are prepared from 1,3-butadiene in 80 mol% yields and >90% selectivity when catalyzed by combinations of halide-free palladium salts and tertiary alkylphosphine ligands of $pK_a > 8$, solubilized in *N*-heterocyclics and tertiary arylamines of moderate base strength (e.g., quinoline and *N*,*N*-diethylaniline). The related palladium(II) acetate-triphenylphosphine couple in isoquinoline/2-propanol allows continued improved activity upon recycle and turnover number exceeding 2×10^3. Concurrent C_5 and C_9 acid syntheses are possible with $Pd(OAc)_2$-DIPHOS. The importance of counterion and Group VB donor ligand structure together with preferred solvent properties are discussed in relation to palladium carbonylation performance and inactivating side reactions.

INTRODUCTION

1,3-Butadiene is predicted (*1*) to be an increasingly important petrochemical building block in the 1980s; continuing our studies of palladium carbonylation chemistry (*2*), we report here an examination of butadiene conversion to carboxylic acid derivatives. Particular emphasis has been given to identifying those parameters which ensure long-term catalyst activity for the palladium and thereby high turnover numbers and multicycle syntheses.

Several research groups have demonstrated the versatility of palladium as a carbonylation catalyst (*2*–*7*). 3-Pentenoate esters have been prepared in >90% selectivity (Eq. 1) using halide-containing palladium salts in alkanols (*6*) and subsequently Tsuji has extended this synthesis to other β,γ-unsaturated acid esters (*7*). Palladium is also useful in diene oligomerization, e.g., the di- and trimerization of 1,3-butadiene to *n*-octatrienes and *n*-dodecatetraenes (*8*, *9*), as well as the coupling of asymmetric conjugated dienes to specific head-to-tail (*10*) and tail-to-tail oligomers (*11*). Combining both functions, a further class of reaction, reported first by Billups in 1971 (*12*), involves the one-step dimerization-carbonylation of 1,3-butadiene to 3,8-nonadienoate esters (Eq. 2) catalyzed by halide-free palladium complexes suspended in a suitable alkanol.



(1)

(2)

Many times, however, there are problems associated with syntheses (1) and (2), particularly regarding the long-term activity of the palladium. In the first place,

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completion of each catalyst cycle generally involves a reductive elimination step (of a Pd-acyl intermediate) that yields Pd(O) plus product acid derivative (*13*). Here ligands such as diene, CO, PR_3, and solvent are needed to stabilize the Pd(O) and satisfy the coordination number, otherwise inactive species (e.g., palladium metal) form that can no longer contribute to the catalytic cycle. A second problem, common to palladium carbonylation chemistry, is nucleophilic attack upon Pd-diene intermediates by OH^-, OR^-, etc., where the diene undergoes palladation (*3*, *13*) and subsequent decomposition or further transformation yields Pd(O) as a by-product. Again, in the absence of suitable stabilizing ligands the only means of preventing build-up of inactive palladium is through the addition of an oxidant, e.g., Cu(II) or Fe(III).

Our purpose has been to develop processing for the multicycle synthesis of nonadienoic and pentenoic acid esters from 1,3-butadiene where the soluble palladium catalyst displays both high specific activity and extended life due to the suppression of inactivating side reactions. We have demonstrated (*15*) that 3,8-nonadienoate esters may be prepared in 80 mol% yields and >90% selectivity using combinations of halide-free palladium salts with tertiary monodentate alkylphosphine ligands of $pK_a > 8$ solubilized in tertiary arylamine and heterocyclic amine solvents of dissociation constants greater than 10^{-7}. Continued improved specific activity is realized in multicycle batch experiments using isoquinoline/2-propanol solutions of palladium acetate-triphenylphosphine, where turnover numbers exceed 2×10^3. Furthermore, approximately, equimolar quantities of C_5 and C_9 acid derivatives may be prepared concurrently during 1,3-butadiene carbonylation catalyzed by halide-free palladium salts with bidentate Group VB donor ligands [e.g., bis(1,2-diphenylphosphino)-ethane] again solubilized in *N*-heterocyclic solvents. The roles played by the counterions, tertiary donor ligands, and solvent media in maintaining this palladium carbonylation activity are discussed in relation to possible mechanisms.

RESULTS

Problems encountered in prior syntheses of nonadienoate esters from 1,3-butadiene (*12*, *16*) include (a) competing precipitation of palladium metal (and therefore short catalyst life), (b) low solubility of the $Pd(OAc)_2$ precursor in the butadiene/alkanol reactants, and (c) low reaction rates. Two approaches have been taken in this work to improve palladium catalyst performance and achieve multicycle syntheses. The first has been to introduce various inert solvent media and the second to modify the metal center by adjusting coordinated ligand structure, Pd:ligand ratios, CO pressure, etc.

Solvent Screening

Simple palladium salts such as palladium(II) acetate and palladium(II) chloride are moderately soluble in a broad range of liquid amines, including *N*-heterocyclics such as quinoline, isoquinoline, pyridine and the lutidines, aliphatic polydentate amines such as tetraethylenepentamine, and arylamines such as aniline and its derivatives. Amides such as *N*,*N*-dimethylformamide and pyrrolidone derivatives are also effective solvents (*15*). Subsequent carbonylation studies show many of the catalyst problems $a \rightarrow c$ identified above can be overcome when syntheses are conducted in tertiary amine solvent media. Table 1 provides a side-by-side comparison of the performance of two catalyst precursors, $Pd(OAc)_2$-$2PPh_3$ and $Pd(OAc)_2$-$2PBu_3$, where isopropyl 3,8-nonadienoate is prepared in the presence and absence of tertiary amine. Experiments 10 and 12 are baseline cases where 2-propanol is present in large excess and is the primary solvent (*16*). Experiments 1–9 and 11 are conducted in the presence of a constant volume of tertiary amine. For each of the added solvents, e.g., isoquinoline, lepidine, pyridine, 2-ethylpyrazine, *N*-methylindole, *N*,*N*-diethylaniline, and *N*,*N*-dimethyl-*p*-toluidine, the following improvements in palladium catalyst performance are evident:

(1) Increased 3,8-nonadienoate ester yield, basis butadiene charged (see column 4).

(ii) Improved selectivity to desired linear C_9-acid ester (column 5). Selectivity is understood here to be the ratio of total isopropyl 3,8-nonadienoate ester formed as a function of the total nonadienoate plus pentenoate esters.

(iii) Greater catalyst stability, as measured by the percentage palladium remaining in solution after completion of the syntheses (column 7).

(iv) Improved ratio of carbonylation products (nonadienoate and pentenoate esters) relative to less desirable diene oligomers (vinylcyclohexenes and *n*-octatrienes) also present in the product mix (see column 6).

More detailed studies of the importance of solvent structure upon the performances of the palladium catalysts showed the improved characteristics i–iv are best realized with two classes of tertiary amine solvents. These are high-boiling tertiary amines of moderate base strength, i.e., having dissociation constants greater than 10^{-7}. They include heterocyclic amines such as quinoline, isoquinoline, lepidine, quinaldine, acridine, and the lutidines (Table 1),

TABLE 1

Butadiene Dimerization/Carbonylation—Effect of Solvent Media[a]

Expt	Pd-catalyst composition	Amine solvent	Isopropyl nonadienoate		Ester/ oligomer ratio[d]	Recovered Pd (%)[e]
			Yield (mol%)[b]	Selectivity (%)[c]		
1	$Pd(OAc)_2$-$2PBu_3$	Quinoline	62	91.4	5.3	>95[f]
2	$Pd(OAc)_2$-$2PBu_3$	Lepidine	66	96.2	6.2	>95
3	$Pd(OAc)_2$-$2PBu_3$	Quinaldine	57	95.9	4.3	50
4	$Pd(OAc)_2$-$2PBu_3$	Pyridine	55	94.3		88
5	$Pd(OAc)_2$-$2PBu_3$	3,5-Lutidine	63	92.6	4.4	>95
6	$Pd(OAc)_2$-$2PBu_3$	*N*-Methylindole	61	90.8	4.5	93
7	$Pd(OAc)_2$-$2PBu_3$	*N*,*N*-Diethylaniline	63	94.8	6.6	>95
8	$Pd(OAc)_2$-$2PBu_3$	*N*,*N*-Dimethyl-*p*-toluidine	64	96.7	6.2	>95
9	$Pd(OAc)_2$-$2PBu_3$	2-Methylpyrazine	55	94.0	6.6	95
10	$Pd(OAc)_2$-$2PBu_3$	None[g]	47	83.6	3.8	28
11	$Pd(OAc)_2$-$2PPh_3$	Isoquinoline	45	96.8	3.4	38
12	$Pd(OAc)_2$-$2PPh_3$	None[g]	31	88.1	2.3	9.3

[a] Charge mixture: 1.34 mmol $Pd(OAc)_2$; 0.37 mol C_4H_6; 60 ml tertiary amine/2-propanol (2:1, v/v). Carbonylation conditions: 110°C; 48 atm initial pressure; 18 hr.

[b] Isopropyl 3,8-nonadienoate yield basis butadiene charged, estimated by glc.

[c] Selectivity basis: isopropyl 3,8-nonadienoate yield as a function of total $C_5 + C_9$ acid ester.

[d] Ratio basis: total $C_5 + C_9$ acid ester/total C_8-oligomer fraction in crude liquid product.

[e] Percentage Pd remaining in solution after butadiene carbonylation basis Pd originally charged.

[f] Similar Pd recovery after allowing product solution to stand for 60 days.

[g] Charging 60 ml of 2-propanol as the Pd-catalyst solvent plus coreactant.

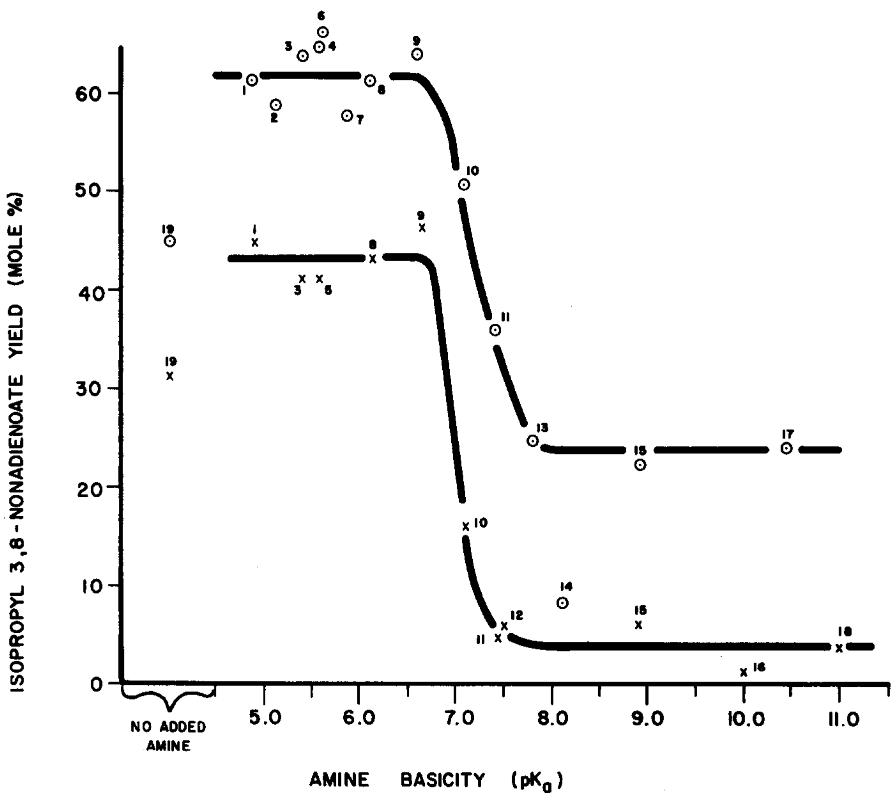
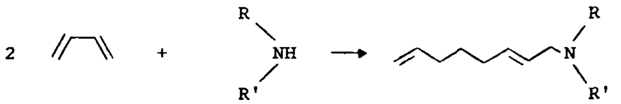


FIG. 1. Palladium catalyst activity versus amine solvent structure. (a) Catalyst precursor: ×, $Pd(OAc)_2$-$2PPh_3$; ⊙, $Pd(OAc)_2$-$2PBu_3$. Solvent: 1, quinoline; 2, *N,N*-dimethylaniline; 3, isoquinoline; 4, *N,N*-dimethyl-*p*-toluidine; 5, acridine; 6, lepidine; 7, quinaldine; 8, 3,5-lutidine; 9, *N,N*-diethylaniline; 10, *N*-methylimidazole; 11, *N*-methylmorpholine; 12, 2,4,6-collidine; 13, *N*-ethylmorpholine; 14, *N,N'*-dimethylpiperazine; 15, *N,N*-dimethylbenzylamine; 16, tetraethylenepentamine; 17, *N*-ethylpiperidine; 18, triethylamine; 19, no amine solvent added. (b) pK_a data taken from Refs. (*29–31*).

as well as tertiary aromatic amines such as *N,N*-dimethylaniline, *N,N*-dimethyl-*p*-toluidine, and *N,N*-diethylaniline. While the data in Table 1 are illustrative of a 2:1 amine:isopropanol mix, the concentration of tertiary amine in the reaction liquid may vary from at least 30 to 90% without inhibiting this improved catalysis.

Figure 1 provides 3,8-nonadienoate yield data for 18 different amine solvent systems. It confirms that ester yields are improved for both the $Pd(OAc)_2$-$2PPh_3$ and $Pd(OAc)_2$-$2PBu_3$ catalyst precursors solubilized in tertiary amines of $pK_a < 7$ (data points 1 → 9) over the baseline case (*19*), with no amine solvent. *N*-Methylimidazole is a marginal situation (point 10), but for all tertiary nitrogen bases of $pK_a > 7$, such as *N*-methylmorpholine, 2,4,6-collidine, *N,N*-dimethylbenzylamine, *N*-ethylpiperidine, and triethylamine (*11–18*) there is supression of ester yields, in some cases by a factor of 4 or more. Butadiene dimerization to vinylcyclohexenes and *n*-octatrienes (*9, 17*), on the other hand is not inhibited by these stronger amines and with triethylamine, for example, the ratio of ester product/C_8-oligomer is ca. 0.2. Isomerization to isopropyl 2,7-nonadienoate is also observed. Primary and secondary amines such as imidazole, 8-aminoquinoline, and tetraethylenepentamine lead to much reduced carbonylation activity (*15*) in part due to competing *n*-octadienyl amine formation (Eq. 3, Refs. *9*, *18*).


(3)

Palladium Catalyst Structure

An extensive range of palladium salt combinations with Group VB donor ligands has also been screened for 1,3-butadiene dimerization-carbonylation. Comparative data are summarized in Tables 2 and 3. Highest yields of 3,8-nonadienoate ester are afforded with halide-free palladium salts, such as palladium acetate, in combination with more basic tertiary phosphines of $pK_a > 8$ such as tri-*n*-butylphosphine and triethylphosphine. Where 2-propanol is the nucleophilic coreactant, these catalyst combinations allow isopropyl 3,8-nonadienoate yields exceeding 60 mol% per pass (Expt 18, 20) or 80 mol% basis butadiene converted. Selectivity to nonadienoate ester is 90 to 91 wt%, the minor carbonylation product in this case being isopropyl 3-pentenoate (Eq. 1). Again the principal competing reaction is butadiene dimerization to C_8-olefin, primarily 4-vinylcyclohexene, plus smaller amounts of 1,3,7-octatriene. After injection of the 1,3-butadiene into the palladium catalyst solution, the concentration of vinylcyclohexenes increases rapidly (Fig. 2), but then reverse Diels-Alder apparently becomes important and the concentration of cyclic C_8s remains

TABLE 2

Butadiene Dimerization/Carbonylation—Effect of Pd Catalyst Structure-I[a]

Expt	Catalyst composition	Isopropyl nonadienoate		Total ester/C_8-oligomer ratio (wt)[d]
		Yield (mol%)[b]	Selectivity (%)[c]	
13	$Pd(OAc)_2$-$2P(OPh)_3$	8.0	82.6	4.3
14	$Pd(OAc)_2$-$2P(OEt)_3$	7.7	>99	0.6
15	$Pd(OAc)_2$-$2P(p\text{-}Cl\cdot C_6H_4)_3$	11.8	>99	0.6
16	$Pd(OAc)_2$-$2PPh_3$	44.7	96.8	3.4
17	$Pd(OAc)_2$-$2P(p\text{-}CH_3\cdot C_6H_4)_3$	52.5	96.3	4.9
18	$Pd(OAc)_2$-$2P(n\text{-}Bu)_3$	61.6	91.4	5.3
19	$Pd(OAc)_2$-$2P(c\text{-}C_6H_{11})_3$	55.1	96.8	4.8
20	$Pd(OAc)_2$-$2PEt_3$	62.8	90.8	4.4
21	$Pd(OAc)_2$-$2P(o\text{-}CH_3\cdot C_6H_4)_3$	10.8	92.8	1.0
22	$Pd(OAc)_2$-DIPHOS[e]	13.0	32[f]	2.9
23	$Pd(OAc)_2$-DIARS[e]	0.7	74	0.1
24	$Pd(OAc)_2$-$2AsMe_3$	1.2	>95	<0.1
25	$Pd(PPh_3)_2(OAc)_2$	33.6	96.9	3.6
26	$Pd(OAc)_2$-$2P(n\text{-}Bu)_3$-5NaOAc	57.1	92.4	5.3
27	$Pd(Acac)_2$-$2P(n\text{-}Bu)_3$	41.3	91.1	2.8
28	$Pd(\pi\text{-}Allyl)(OAc)_2$-$2P(n\text{-}Bu)_3$	31.2	81.8	3.0

[a] Run conditions: [Pd], 22.3 m*M*; C_4H_6, 0.37 mol; quinoline/2-propanol (2:1, v/v), solvent; 110°C; 48 atm initial pressure; 18 hr.

[b] Isopropyl 3,8-nonadienoate yield basis butadiene charged (theory), estimated by glc.

[c] Selectivity basis: isopropyl 3,8-nonadienoate yield/total ester yield.

[d] Total isopropyl C_9 + C_5 acid esters/total C_8-oligomer in liquid product.

[e] DIPHOS, bis(1,2-diphenylphosphino)ethane; DIARS, bis(1,2-diphenylarsino)ethane.

[f] Yield of isopropyl 3-pentenoate, 16 mol%.

TABLE 3

Butadiene Dimerization/Carbonylation—Effect of Pd-Catalyst Structure-II[a]

Expt	Catalyst composition	Added amine solvent	Isopropyl ester yield (mol%)	
			Nonadienoate	Pentenoate
29	Pd(OAc)$_2$-2P(*n*-Bu)$_3$	Quinoline	62	2.1
30	Pd(NO$_3$)$_2$·xH$_2$O-2P(*n*-Bu)$_3$	Quinoline	55	2.7
31	PdCl$_2$-2PPh$_3$	Isoquinoline	10	16
	Recycle	Isoquinoline	13	13
	Recycle	Isoquinoline	15	12
32	Pd(OAc)$_2$-DIPHOS	Isoquinoline	14	12
	Recycle	Isoquinoline	29	9.0
	Recycle	Isoquinoline	39	6.1
33	Pd(OAc)$_2$-5DIPHOS	Quinoline	< 0.1	0.1
34	PdCl$_2$-DIPHOS	Isoquinoline	1.2	1.9
35	PdCl$_2$-2PPh$_3$	None	1.0	1.3

[a] Run conditions: Pd, 1.34 mmol; C_4H_6, 0.37 mol; 48 atm initial pressure; 110°C; 18 hr.

[b] Terms as defined in Table 2.

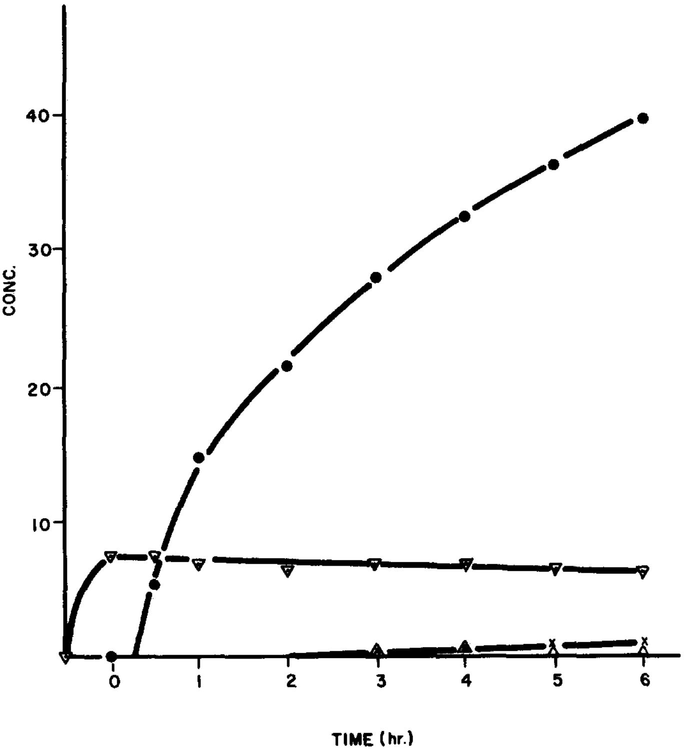


FIG. 2. Typical reaction profile for 1,3-butadiene dimerization–carbonylation. ●, Isopropyl nonadienoate; ×, isopropyl pentenoate; ▽, vinylcyclohexene; △, *n*-octatriene. (a) Zero time corresponds to time reaction mixture reached 110°C after heat was applied to autoclave. If the catalyst solution is heated to 110°C prior to butadiene addition some Pd precipitation occurs. (b) Charge mixture: Pd(OAc)$_2$, 2.67 mmol; PBu$_3$, 5.34 mmol; C_4H_6, 0.18 mol; 90 ml quinoline/isopropanol (2:1, v/v). Run at constant pressure, 54 atm.

essentially unchanged throughout the remainder of the carbonylation sequence. Smaller quantities of isopropyl 3-pentenoate and 1,3,7-octatriene are detected after ca. 2 hr.

For a series of palladium acetate–tertiary monodentate phosphine combinations, solubilized in quinoline (Table 2), ligands of similar spatial size but increasing basicity (*19*) lead to improved nonadienoate ester yields in the order:

$$\mathrm{P(OPh)_3} < \mathrm{P}(p\text{-Cl}\cdot\mathrm{Ph})_3 < \mathrm{PPh_3} < \mathrm{P}(p\text{-CH_3}\cdot\mathrm{Ph})_3 < \mathrm{P}(n\text{-Bu})_3 \quad (4)$$

This relationship is displayed graphically in Fig. 3; highest specific activities are reached then with the palladium acetate-tri-*n*-butylphosphine and triethylphosphine combinations. Similar ester yields are realized whether the palladium catalyst is prepared or generated *in situ* (Expts 16 and 25).

Ligand steric properties also seriously influence palladium catalyst performance, as illustrated here by the comparative experiments in Table 2. In particular, we note a fivefold drop in nonadienoate ester yield upon increasing the triarylphosphine bulk from tri-*p*-tolylphosphine (cone angle 145°, Ref. *20*) to tri-*o*-tolylphosphine (cone angle 194°). A less dramatic yield change is recognized for the alkylphosphine series (Eq. 5) as the ligand cone angle is lowered from 179 to 130°.

$$\mathrm{P}(c\text{-C_6H_{11}})_3 < \mathrm{P}(n\text{-C_4H_9})_3 \cong \mathrm{P(C_2H_5)_3} \quad (5)$$

Softer ligand bases, such as the triorganoarsines, are far less effective than the analogous phosphines (cf. Expts 24 and 20), while C_9-acid ester yields are drastically reduced when triphenylphosphine is replaced by triphenylphosphine oxide.

Concomitant C_5/C_9 Acid Ester Syntheses

Concomitant syntheses of the pentenoate and nonadienoate esters is possible with

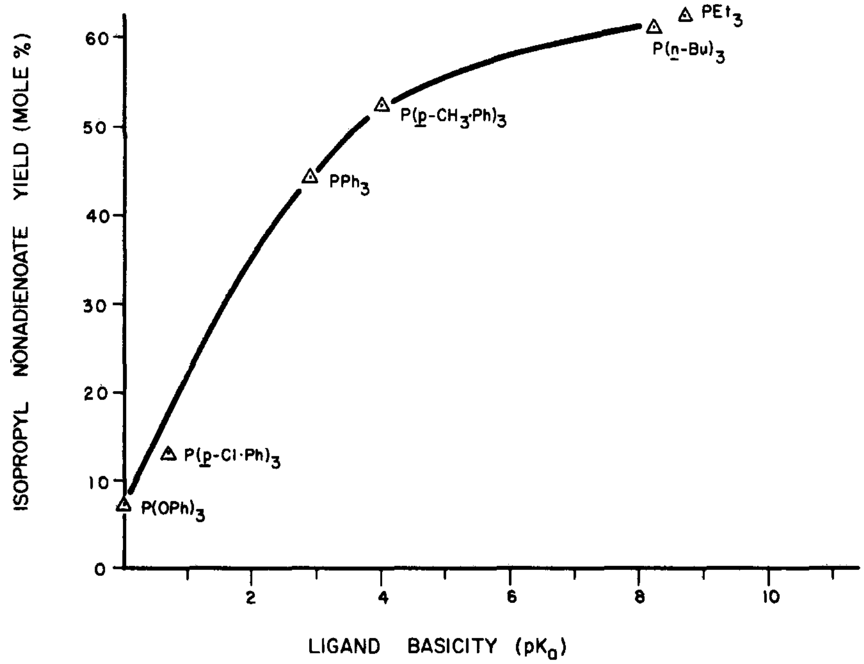


FIG. 3. Palladium catalyst activity versus Group VB donor ligand structure. Catalyst precursor: $\mathrm{Pd(OAc)_2\text{-}2PR_3}$.

two other perturbations in the Pd-catalyst structure. First, for the PdX_2–$2PR_3$ series solubilized in quinoline/2-propanol, preparative quantities of both isopropyl 3-pentenoate and 3,8-nonadienoate esters are achieved only where the counterion X is chloride (Tables 2 and 3). The sensitivity of 1,3-butadiene carbonylation to the presence of halogen has already been noted (*14*, *16*, *18*), but in a comparative experiment, $PdCl_2$–$2PPh_3$ in the absence of tertiary amine solvent yielded C_8-olefin almost exclusively with only trace quantities of carbonylation products (cf. Expts 31 and 35).

A second route to $C_5 + C_9$ acid derivatives is through the use of halide-free palladium salts in combination with polydentate phosphines. Table 3 illustrates the case of $Pd(OAc)_2$ combined with bis-(1,2-diphenylphosphino)ethane (DIPHOS), solubilized in either quinoline or isoquinoline. Again the advantages of the $Pd(OAc)_2$-DIPHOS system in quinoline (Expt 32) over the corresponding catalyst in the absence of the amine include (a) improved yields of both pentenoate and nonadienoate esters, (b) C_5/C_9 ratios closer to unity, and (c) improved palladium catalyst performance upon recycle, even after product ester isolation (*15*).

π-Allyl and chelating acetylacetonate ligands tend to suppress the carbonylation rate but nonadienoate esters remain the major product (Table 2). Of particular note, however, palladium in the presence of *both* chloride ion and bidentate DIPHOS does not yield preparatively significant quantities of either C_5 or C_9 acid derivatives (Expt 34), likewise, $Pd(OAc)_2$ in the presence of excess DIPHOS (Expt 33).

Catalyst Recycle Studies

Preliminary recycle studies for the $Pd(OAc)_2$-$2PPh_3$ catalyst suspended in excess 2-propanol (i.e., in the absence of tertiary amine solvent) showed that under conditions set to favor dimerization–carbonylation (*12*, *16*), yields of C_9-acid ester drop precipitously with each successive catalyst cycle (Fig. 4, X data points) and much of the palladium is in an insoluble form after three cycles (in fact the product liquid contained only 3% of the Pd originally charged). By contrast, the potential long life of the $Pd(OAc)_2$-$2PPh_3$ catalyst solubilized in *N*-heterocyclic solvents is illustrated by the O data points in Fig. 4. Here a single, small sample of palladium acetate (1.34 mmol, 0.14 g Pd) plus triphenylphosphine are solubilized in an isoquinoline/2-propanol mix (60 ml, 2:1 v/v) and, after pressuring with butadiene (20 g) and CO, isopropyl nonadienoate synthesis is carried out as described (see Experimental). Carbonylation of successive butadiene samples is conducted likewise over 32 Pd catalyst cycles using the same Pd charge. Following every third or fourth cycle the nonadienoate ester is recovered by fractional distillation *in vacuo* from the crude liquid mix. The distillate ester samples still contain some isoquinoline but are free of small quantities of pentenoate ester and vinylcyclohexene by-products.

Yield and selectivity data are given in Fig. 4; the scatter is due, at least in part, to changes and modifications made to the experimental procedure during the 32 cycles. In particular, to define limiting conditions better, no make-up triphenylphosphine is added in the sequence from cycles 6 to 13, while the quantity of butadiene charged each cycle is halved during 29 through 31.

It should also be noted that:

(i) Over 32 cycles there is no call for palladium catalyst regeneration. Overall activity, basis yield data, drops only a few percentage points and remains close to that of the fresh material under otherwise standard operating conditions.

(ii) The effective specific activity of the palladium appears actually to improve

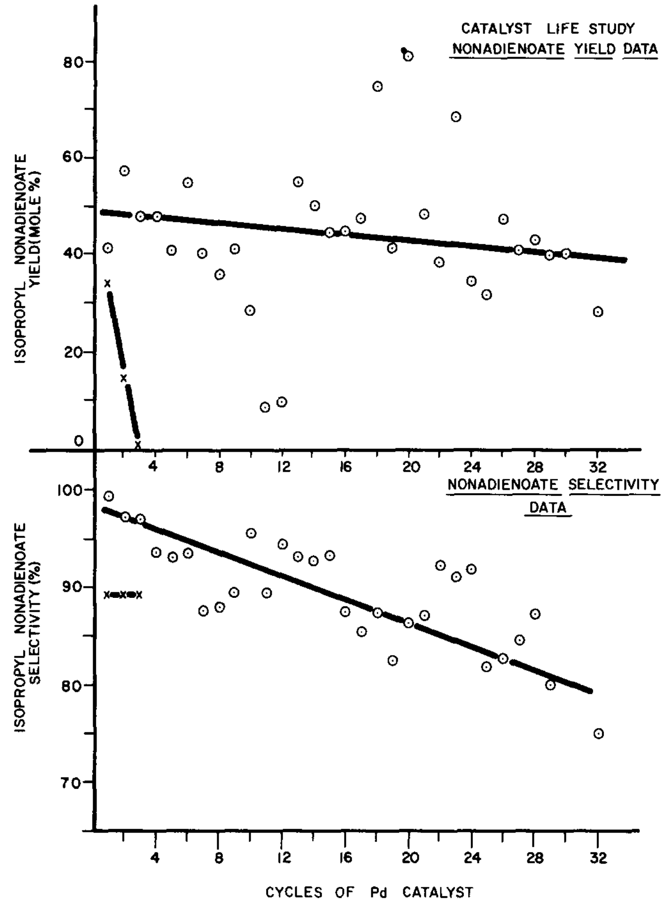


Fig. 4. Palladium catalyst life. ○, Solvent isoquinoline added; ×, No amine solvent. Least squares plot —.

with successive cycling since there are in fact significant losses in palladium over the 32 cycles (54%) on account of mechanical handling, sampling, etc. This mechanical loss is nearly compensated for by the improved specific activity, so that the net effect is only a modest decline in performance per cycle.

(iii) Turnover numbers in this and similar experimental series exceed 2×10^3.

After the 32 cycles, elemental and spectroscopic analyses of the red liquid residue (18.5 g) confirmed the presence of soluble palladium salt (726 ppm), triphenylphosphine oxide (P = 1.36%; ν, 1180, 118, 750, 725, and 688 cm^{-1}) plus low MW polymer (C, 82.0%; H, 9.8%).

Similar Pd-catalyst recycle studies show isopropyl nonadienoate can be prepared in 60–65 mol% yields per cycle (basis butadiene charged) using considerably shorter reaction times (5–6 hr) and the $Pd(OAc)_2$-$2PBu_3$ combination. Here the initial [Pd] is 45 m*M* and recovery of palladium in solution after four cycles is >95%.

DISCUSSION

Enhanced palladium catalyst stability during 1,3-butadiene carbonylation, and thereby higher ester yields (Eqs. 1 and 2), coupled with greatly improved catalyst life, are the important features of the amine-solubilized palladium catalyst system described herein. Only tertiary amines

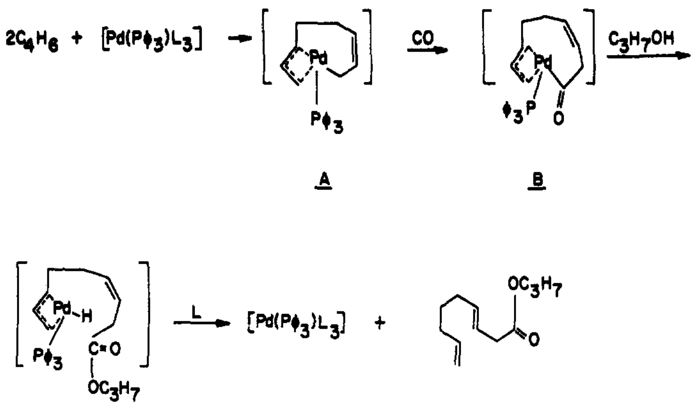
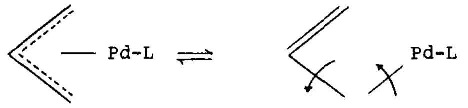


FIG. 5. Reaction scheme for 1,3-butadiene dimerization–carbonylation to isopropyl 3,8-nonadienoate.

of moderate base strength contribute both to the improved palladium salt solubility and stability during carbonylation without obstructing the desired conversions to C_5 and C_9 acid derivatives. Two classes of suitable tertiary amine have been identified in this work, *N*-heterocyclic amines such as quinoline, isoquinoline, lepidine, and 3,5-lutidene and tertiary arylamines such as *N*,*N*-diethylaniline and *N*,*N*-dimethyl-*p*-toluidine (see Table 1). Stronger tertiary amine bases exhibit, in some cases, improved solvation properties but then block ester formation (e.g., triethylamine and *N*,*N*′-dimethylpiperazine, Fig. 1). Primary and secondary amines lead to the formation of 2,7-octadienylamines as a competing reaction (Eq. 3).

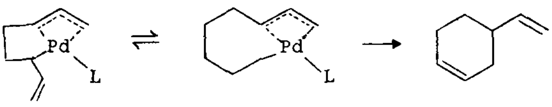
The role of auxiliary ligands in palladium-catalyzed reactions is often of critical importance (*13*). The addition of amines has been noted previously to enhance the rate of diene coupling, e.g., as in the reductive dimerization of isoprene (*10*) and in octadienyl amine (*9*) and ester syntheses (*21*), as well as in the carbonylation chemistry of other Group VIII metals (*22*). However, whereas the more basic tertiary alkyamines, such as triethylamine, are preferred in the case of diene coupling (*9*, *10*, *21*), we find under carbonylation conditions the same amines inhibit 3,8-nonadienoate synthesis (Fig. 1). This failure to produce good yields of C_9 acid ester in the presence of tertiary amines of $pK_a > 7$ is attributed to blocking of available coordination sites on the palladium by the alkylamine during the critical carbonylation steps (see Fig. 5). The synthesis (2) is thought to proceed via coupling of two butadiene units (*4*, *16*) then CO insertion at the σ-allylic position of *A* to generate the octadienediylpalladium phosphine complex *B* which, upon attack by alkoxide ion, collapses *B* and yields the desired 3,8-nonadienoate ester while regenerating the active Pd-catalyst. Among the preferred series of *N*-heterocyclic amine bases there are similar enhancements in ester yields (Fig. 1) even though, for example, pyridine, quinaldine, lepidine, and quinoline, as coordinated ligands, would have very different steric requirements. This leads us to believe that these preferred amine additives are not coordinated to the palladium during the carbonylation. Rather, the primary function of the *N*-heterocycles, and the tertiary arylamines, is to provide stabilization for the palladium in its elimination product $Pd(PR_3)L_3$. Certainly this would be more consistent with the observed differences in Pd stability when solubilized in quinoline versus its *ortho*-methylated homolog, quinaldine (see Table 1, column 7) where there is greater steric hindrance about the nitrogen. A second function of the tertiary amine is to accelerate reduction of the palladium(II) acetate to the catalytically active zero-valent palladium (*13*).

No diene carbonylation has been observed in this work in the absence of tertiary phosphine (*15*, *16*). The introduction of trialkylphosphines should favor the σ-allylic form of *A*, rather than the π-allylic form (*23*), and since the σ-allylic species will more readily undergo CO insertion, it seems likely that displacement of Eq. (6) equilibrium to the right by the more basic alkylphosphines (*19*) is the factor responsible for the observed improved nonadienoate ester yields with increased ligand basicity (Fig. 3).



(6)

Increasing electron-donating ability of the coordinated ligands also favors diene coupling (*10*), as well as the formation of vinyclohexene by-product (*24*). This is particularly true where conditions allow collapse of *A* prior to CO insertion, that is where the carbonylation step is slow (e.g., <100°C, Ref. *15*). Vinylcyclohexenes are consistently the major C_8 by-products in our work. Model studies by Wilke (*23*) indicate that vinylcyclohexene formation is in fact favored by the terminal σ-alkyl, π-allyl form of *A* (Eq. 7) and indeed a basicity ordering similar to Eq. 4 has been noted previously during butadiene cyclodimerization studies with phosphine-substituted nickel complexes (*24*). On the other hand, neither 4-vinylcyclohexene nor *n*-octatrienes (3:1 ratio in the product mix) is readily carbonylated by our catalysts (Table 4), so neither is going to be an important intermediate in C_9-acid ester formation (*12*).



(7)

Rates of butadiene carbonylation and yields of nonadienoate ester are very sensitive to applied CO pressure (*15*, *16*) and CO "insertion" to form *B* is possibly a slow step in Fig. 5. The stereochemical requirements of the palladium appear particularly strict during this insertion process. For example, whereas triorganophosphine-palladium catalysts are known to dimerize isoprene and related alkylated dienes (*10*), preparative quantities of C_9-C_{13} unsaturated acid ester are obtained here only in the case of 1,3-butadiene (Table 4). Similarly, although the steric requirements of the donor phosphine ligands are of modest importance in the reductive dimerization of isoprene (*10*), yields of nonadienoate vary by a factor of 5 or more during replacement of *p*-tolylphosphine by the bulkier *o*-tolylphosphine (Expts 17 and 21, and Eq. 5). Clearly the bulkier organophosphines are blocking one or more coordination sites, but several Pd-P equilibria are involved prior to diene coupling since maximum nonadienoate yields are realized at phosphine:palladium ratios of 2:1 (*15*), versus a single coordination site available on *A* and *B*.

One further, important, benefit of the *N*-heterocyclic and tertiary arylamine solvents is that the palladium-phosphine catalysts are now less sensitive to coreactant nucleophilicity. In contrast to prior studies, primary, secondary, and tertiary aliphatic alcohols, as well as water, may function as coreactants during butadiene dimerization-carbonylation without

TABLE 4

The Carbonylation of Conjugated Dienes/Trienes

Polyene substrate	Palladium catalyst	Solvent	Polyene conv. (%)	Major acid ester products	
				Identity	Yield (mol%)
1,3,7-Octatriene[a]	$Pd(OAc)_2\text{-}2PPh_3$	Isoquinoline	5.7	Isopropyl nonadienoate	0.7
4-Vinylcyclohexene[a]	$Pd(OAc)_2\text{-}2PPh_3$	Isoquinoline	2.0	Isopropyl nonadienoate	0.05
Isoprene[c]	$Pd(OAc)_2\text{-}2PBu_3$	Pyridine	23	None[b]	
Isoprene[d]	$Pd(OAc)_2\text{-}2PBu_3$	Pyridine	83[d]	Isopropyl dimethyl-nonadienoate	1.3
1,3-Pentadiene	$Pd(OAc)_2\text{-}2PBu_3$	Pyridine	<10	None[b]	
2,3-Dimethyl-1.3-butadiene	$Pd(OAc)_2\text{-}2PBu_3$	Pyridine	4.9	None[b]	

[a] Pd, 1.34 mmol; C_8H_{12}, 50 mmol; 110°C; 48 atm initial pressure; 18 hr.

[b] No isopropyl esters detected.

[c] C_5H_8 charge, 185 mmol.

[d] Run at 160°C, considerable C_{10}-diene and polymer formation.

seriously affecting either the nonadienoic acid/ester yield or palladium stability (see Table 5). Furthermore, with primary alcohols, like methanol, there is no evidence for 1-alkoxy-2,7-octadienes (*9*), at least during our 6-hr run times.

Finally, there is the question of C_5 versus C_9 acid formation. Although an excess of weakly coordinating acetate ion has no significant effect upon the relative rate of butadiene carbonylation or the selectivity to nonadienoate ester (Table 2, Expt 26) other more strongly bonding chloride and bidentate phosphine ligands take up coordination positions required by the π-allyl group (*18*, *25*), thereby blocking diallyl-Pd formation (step A, *18*) and favoring monomeric η-allylic complexation and 3-pentenoate ester (Table 3). Medema has pointed out also that there is an important difference in molecular stereochemistry between π-allylpalladium chlo-

TABLE 5

Butadiene Dimerization/Carbonylation—Effect of Coreactant Structure[a]

Pd catalyst composition	Amine solvent	Coreactant structure	Nonadienoate ester			Ester/oligomer ratio
			Identity	Yield (mol%)	Sel. (%)	
$Pd(OAc)_2\text{-}2P(n\text{-}Bu)_3$	Quinoline	2-Propanol	Isopropyl nonadienoate	62	91.4	5.34
$Pd(OAc)_2\text{-}2P(n\text{-}Bu)_3$	Quinoline	Methanol[b]	Methyl nonadienoate	45	93.0	3.31
$Pd(OAc)_2\text{-}2P(n\text{-}Bu)_3$	Quinoline	*t*-Butanol	*t*-Butyl nonadienoate	49	95.8	3.32
$Pd(OAc)_2\text{-}2PPh_3$	Isoquinoline	Ethanol	Ethyl nonadienoate	44	95.5	4.34
$Pd(OAc)_2\text{-}2PBu_3$	Isoquinoline	Water[c]	Nonadienoic acid	50	80[d]	3.4

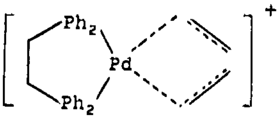
[a] Run conditions: [Pd], 22 mM; C_4H_6, 0.37 mol; quinoline/alkanol (2:1, v/v); 110°C, 48 atm initial pressure; 18 hr.

[b] Run conditions: [Pd] = 45 mM, C_4H_6, 0.18 mol, 6 hr.

[c] Isoquinoline/water (5:1, v/v).

[d] 3-Pentenoic acid also formed in ca. 13% yield, both acids isolated as their esters by treatment with BF_3/MeOH reagent.

ride and π-allylpalladium acetate (*8*). In the chloride the distance between the allyl groups is 7.7 A vs. 2.9 A in the acetate. Mono η^3-allylic palladium complexes of bis(1,2-diphenylphosphino)ethane have been isolated for a variety of dienes (*26*).



Again it is important to note the marked improvement in Pd-catalyst performance upon adding a *N*-heterocyclic solvents such as quinoline (Table 3), and the almost complete suppression of both carbonylation reactions (1) and (2) when additional "blocking" ligands (Cl and DIPHOS) are added, as in the case of the precursors $Pd(OAc)_2$-5DIPHOS and $PdCl_2$(DIPHOS) (Expts 33 and 34).

EXPERIMENTAL

Palladium salts and complexes were purchased from outside suppliers, or, as with (π-allyl)palladium acetate (*27*) and bis(triphenylphosphine)palladium(II) acetate (*28*), prepared according to literature procedures. Standard, *N*-heterocyclic solvents were distilled, dried over Linde 3A molecular sieve, and flushed with nitrogen prior to use. Reaction solutions were prepared directly in the glass liners of the 300-ml pressure reactor under a nitrogen purge. Diene dimerization and/or carbonylation experiments were carried out as outlined below. The extent of reaction and distribution of products were determined by gas–liquid chromatography (glc) using, for the most part, 4 to 6 ft × $\frac{1}{4}$ in. columns of 10% OS-124 liquid phase on 60/80 mesh Chromosorb "G" or "W" programmed from 100 to 210°C (100 cm^3/min He). Solutions containing *N*,*N*-dimethyl-*p*-toluidine and *N*,*N*-diethylaniline were analyzed with a 16 ft × $\frac{1}{8}$ in. column of OV-17. Product polyenes and acid esters were isolated by distillation *in vacuo*, or glc trapping, and identified by one or more of the following techniques: glc, ir, NMR, and elemental analyses.

Isopropyl Nonadienoate Preparation from Butadiene

1. Synthesis procedure. To a suitable glass liner containing 2-propanol (20 ml) and isoquinoline (40 ml) under nitrogen purge is added 0.30 g of palladium acetate (1.34 mmol) and 0.54 g of tri-*n*-butylphosphine (2.68 mmol). The mixture is stirred to dissolve all solids and the clear red solution transferred to the 300-ml autoclave reactor. After sealing and flushing with carbon monoxide, butadiene (20 g, 0.37 mol) is injected from a side-ampoule. The reactor is further pressured with carbon monoxide to 48 atm, heated to 110°C, and held at temperature for 18 hr. At the end of this time the reaction is terminated by rapid cooling.

Gas chromatographic analyses of the clear, deep-red liquid product (86 ml) indicate the following: isopropyl nonadienoate selectivity (among product esters), 91.4%; yield of isopropyl nonadienoate (basis butadiene charged), 61.6 mol%.

Typical off-gas samples show the presence of carbon monoxide (95%), butadiene (2.5%), and CO_2 (0.3%).

2. Recycle of palladium catalyst solution. The recovered liquid product from above is recharged to the autoclave reactor in the glass liner, the reactor again purged with CO, and a second 20-g sample of butadiene injected from the side ampoule. After carbonylation under the conditions described *supra*, the reactor is cooled and another small (ca. 1 ml) sample of product liquid set aside for glc analysis. Carbonylation of a third, and possibly fourth, sample of butadiene (20 g each) is completed after the introduction of additional 2-propanol (10–30 ml).

Typical isopropyl nonadienoate yields per cycle (calculated by glc) are as follows:

Cycle I, 61.6 mol%; Cycle II, 65.2 mol%; Cycle III, 52.9 mol%; Cycle IV, 44.0 mol%.

3. Isopropyl nonadienoate recovery. Following recovery of the crude liquid product (160–170 ml) from the autoclave reactor, it is subject to distillation *in vacuo.* After removal of the light ends, the fraction distilling at 63 to 68°C (0.5–1.0 mm Hg) is substantially isopropyl nonadienoate plus some isoquinoline solvent. The palladium acetate-tri-*n*-butylphosphine catalyst remains behind in the isoquinoline/heavy end bottoms, a deep-red clear liquid. Normally some nonadienoate ester may still be detected in this residuum.

Further purification of the isopropyl nonadienoate distillate fraction, particularly removal of any remaining isoquinoline, may be achieved by solvent extraction, or a second distillation under more rigorous conditions.

Typical recovery data are as follows: isopropyl nonadienoate, isolated yield: 83 to 86% of theoretical, calculated by glc; palladium balance, after four cycles: 92 to 103 wt% of Pd charged.

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