Homogeneous Catalysis in the Reactions of Olefinic Substances. V. Hydrogenation of Soybean Oil Methyl Ester with Triphenylphosphine and Triphenylarsine Palladium Catalysts[1, 2]

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Abstract

Some palladium complexes containing coordinated triphenylphosphine or arsine have been found to be effective and selective catalysts in the homogeneous hydrogenation of soybean oil methyl ester. The characteristic features of the catalysis are 1) isomerization of *cis* double bonds to *trans* double bonds, 2) migration of isolated double bonds to form conjugated dienes, 3) selective hydrogenation of poly olefines to mono olefines without hydrogenation of mono olefine, 4) ester exchange of methyl ester to butyl ester, 5) effective hydrogenation and isomerization by methanol in the absence of elemental hydrogen.

The catalytic activity of a variety of palladium complexes decreases in the following order: $(\phi_3P)_2PdCl_2 + SnCl_2{\cdot}2H_2O > (\phi_3P)_2PdCl_2 + GeCl_2 > (\phi_3P)_2Pd(CN)_2 > (\phi_3As)_2Pd(CN)_2 > (\phi_3P)_2PdCl_2 \gg (\phi_3As)_2PdCl_2$. However, neither K_2PdCl_4 with $SnCl_2{\cdot}2H_2O$ nor $(\phi_3P)_2Pd(SCN)_2$ was effective for hydrogenation. The hydrogenation and isomerization of soybean oil methyl ester have been examined under various conditions using a mixture of $(\phi_3P)_2PdCl_2$ and $SnCl_2{\cdot}2H_2O$. Under nitrogen pressure, in benzene and methanol as a solvent, both isomerization and hydrogenation of soybean oil methyl ester proceeded less effectively than under hydrogen pressure.

Introduction

THE HYDROGENATION of vegetable oils, because it results in materials with new properties and increased values and utility, finds wide industrial application. Commonly, heterogeneous catalysis is employed, and there are few examples of hydrogenation with homogeneous catalysts. However, homogeneous catalysts may be expected to effect hydrogenations of higher selectivity and specificity than heterogeneous catalysts. Reactions of olefinic compounds have been observed under conditions of hydroformylation (oxo-reaction) (1). Homogeneous hydrogenation of unsaturated fatty acids have been investigated using iron carbonyl (2,3) and pentacyanocobaltate(II) ion (4,5).

In a previous report (6), hydridoplatinum complexes were described and it was shown that mixtures of these complexes and tin(II) chloride are effective in the hydrogenation of soybean oil methyl ester (7). In this report, the methods of preparation of several palladium complexes containing triphenylphosphine or arsine are described. The hydrogenation of soybean oil methyl ester was carried out with these palladium complexes as catalysts, and the catalytic effects of such complexes are discussed.

Experimental

Preparation of Dichloro-Bistriphenylphosphine-Palladium (II), $(Ø_3P)_2PdCl_2$ (8)

A solution of palladium chloride (3.0 g, 17.0 mM) in water (150 ml) and concentrated hydrochloric acid (37%, 0.5 ml) was added slowly, with constant stirring, to a warm (ca. 60C) solution of triphenylphosphine (9.0 g, 34.5 mM) in ethanol (300 ml). A yellow powder separated immediately. The reaction mixture was kept at 60C for 3 hr with constant stirring. The precipitate was filtered and washed with hot water (100 ml), hot ethanol (100 ml), and finally with ether (100 ml). An almost quantitative yield (11.6 g, 97%) of dichloro-bistriphenylphosphine-palladium(II) was obtained. This product (1.5 g) ws purified by dissolving it in warm chloroform (50 ml) and precipitating it by addition of n-heptane (150 ml). The pure product was dried over phosphorus(V) oxide at 100C in vacuo. It decomposed at 298–302C.

Anal.: Calcd. for $C_{36}H_{30}Cl_2P_2Pd$: C, 61.57; H, 4.31; Cl, 10.13.

Found: C, 61.38; H, 4.37; Cl, 10.13.

This material is soluble in chloroform, sparingly soluble in benzene and methanol, but insoluble in water, acetone, diethyl ether, carbon tetrachloride and n-heptane.

Preparation of Dicyano-Bistriphenylphosphine-Palladium (II), $(Ø_3P)_2Pd(CN)_2$

Dichloro-bistriphenylphosphine-palladium (II) (3.0 g, 4.3 mM) was added to a solution of potassium cyanide (0.06 g, 9.2 mM) in methanol (150 ml) and the mixture was stirred at 50C for 3 hr. White crystals (2.83 g) separated, were filtered, washed with water and dissolved in chloroform (200 ml). The insoluble residue (0.63 g) was removed by filtration. Upon adding diethyl ether (150 ml) to the filtrate, white crystals (2.1 g, 72%) having a melting point of 330–333C (dec) were obtained. The crystals were dried over phosphorus (V) oxide in vacuo at 100C. The IR spectrum of this material (in Nujol or HCBD mull) shows the characteristic C≡N vibration at 2125 cm^{-1}

Anal.: Calc. for $C_{38}H_{30}N_2P_2Pd$; C, 66.79; H, 4.43; N, 4.10.

Found: C, 66.12; H, 4.41; N, 4.09.

The cyano-complex is soluble in chloroform and in a mixture of benzene and methanol, sparingly soluble in benzene or methanol alone, and insoluble in water, diethyl ether, acetone, carbon tetrachloride and n-heptane.

Preparation of Dithiocyanato-Bistriphenylphosphine-Palladium (II), $(Ø_3P)_2Pd\ (SCN)_2$

To a solution of potassium thiocyanate (0.9 g, 9.3 mM) in ethanol (180 ml) was added dichlorobistriphenylphosphine-palladium(II) (3.0 g, 4.3 mM). The mixture was kept at 60C with constant stirring

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[1] This work was done under contract with the USDA.

[2] Earlier articles in the series are: I, Inorg. Chem. *4*, 1618 (1965); II, Proceedings of the Symposium on Coordination Chemistry (Tihany, Hungary, 1964), Edited by M. T. Beck, Budapest, 1965; III, JAOCS *43*, 337 (1966); IV, Advances in Chemistry Series, American Chemical Society, in press.

for 5 hr. The yellow crystals (3.15 g) which separated were filtered and washed successively with water, ethanol, and diethyl ether. The product (3.15 g) was dissolved in boiling chloroform (300 ml). Diethyl ether (200 ml) was added to precipitate yellow crystals (0.54 g) having mp 244–246C (dec). These were dried over phosphorus(V) oxide in vacuo at 100C. This material shows the SCN vibration at 2080 cm^{-1} (in Nujol or HCBD mull).

Anal.: Calc., for $C_{38}H_{30}N_2S_2P_2Pd$; C, 61.06; H, 4.06; N, 3.61.

Found: C, 60.62; H, 4.06; N, 3.56.

The total yield was 2.97 g, 91%. The material is slightly soluble in chloroform, very sparingly soluble in benzene and methanol, and insoluble in water, diethyl ether, acetone, carbon tetrachloride, and n-heptane.

Preparation of Dicyano-Bistriphenylarsine-Palladium(II), $(Ø_3As)_2PdCl_2$

To a solution of triphenylarsine (1.73 g, 5.6 mM) in ethanol (50 ml), kept at 60C and constantly stirred, was added a solution of palladium(II) chloride (0.5 g, 2.8 mM) in water (25 ml) containing three drops of concentrated hydrochloric acid. A yellow powder separated immediately. The reaction mixture was stirred at 60C for 1 hr. The powder was then filtered and washed successively with hot water, hot ethanol and diethyl ether. The yellow powder (2.20 g, 90%) was dried over phosphorus (V) oxide in vacuo at 100C. mp, 275–277C (dec).

Anal.: Calc., for $C_{36}H_{30}Cl_2As_2Pd$; C, 54.76; H, 3.83; Cl, 8.97.

Found: C, 55.62; H, 3.86; Cl, 8.95.

This yellow powder (2.2 g) was dissolved in chloroform (60 ml) and precipitated by the addition of diethyl ether (50 ml). Orange colored crystals (2.06 g) melting at 278–280C (dec) were obtained.

Anal.: Found: C, 54.67; H, 3.86; Cl, 9.27.

This material is soluble in chloroform and sparingly soluble in benzene and methanol, but insoluble in water, acetone, carbon tetrachloride and n-heptane.

Preparatoin of Dichloro-Bistriphenylstibine-Palladium(II) $(Ø_3As)_2Pd(CN)_2$

A solution of dichloro-bistriphenylarsine-palladium-(II) (2.0 g, 2.3 mM) and potassium cyanide (0.326 g, 5.0 mM) in benzene (60 ml) and methanol (30 ml) was stirred at room temperature for 3 hr. The solution was filtered and treated with 30 ml of methanol. Upon standing overnight, the solution yielded 1.68 g of white crystals. These were filtered, washed successively with water, methanol, and diethyl ether. The product (1.68 g) was recrystallized three times from a mixture of benzene and methanol. The white crystals were dried over phosphorus(V) oxide in vacuo at 100C. They melted at 209C, with decomposition. They show the C≡N vibration at 2123 cm^{-1} (in Nujol or HCBD mull).

Anal.: Calc., for $C_{38}H_{30}N_2As_2Pd$; C, 59.18; H. 3.92; N, 3.63.

Found: C, 58.59; H, 3.92; N, 3.31.

Preparation of Dichloro-Bistriphenylstibine-Palladium (II), $(Ø_3Sb)_2PdCl_2$

This material was prepared by the method of Chatt and Wilkins (9).

Materials Used for Hydrogenation

The soybean oil methyl ester was prepared from commercial soybean oil, which was purified, hydrolyzed and finally esterified (10). This ester (7) had N_d^{25}, 1.4543 and iodine value 126.8, as determined by Hanus method (11). Methyl oleate was obtained from the Hormel Institute, University of Minnesota.

Hydrogenation Using Palladium Complexes as Catalysts

The hydrogenation of soybean oil methyl ester was carried out as previously described (7).

Hydrogenation of Olefins Using Palladium Catalysts

Hydrogenation of pure olefinic esters was carried out using palladium complexes as catalysts under various conditions as shown in Table II. Methyl oleate (1.5 g, 4.1 mM) was treated with the palladium complex (0.63 mM) and tin(II) dichloride dihydrate or germanium(II) chloride (4.4 mM).

Analysis by IR Spectroscopy (13)

The IR absorption of the esters containing isolated double bonds was measured by the standard method on a Beckman IR5A spectrophotometer using a 1 mm KBr cell. The amount of isolated *trans* double bond was evaluated by using elaidate as a standard. The mean error in the absorbance curve for the primary standard is ±1.6%. Partially hydrogenated ester shows absorption bands at 947 and 987 cm^{-1}, characteristic of conjugated diene (14).

Analysis by Gas Chromatography

Gas chromatographic analyses were carried out on a 10 ft × 1/8 in copper column packed with 20% diethyleneglycol succinate or 20% ethyleneglycol succinate on Chromosorb W (60/80 mesh). A Wilkin's Aerograph Hy-Fi flame ionization detector was employed. Analyses on the diethyleneglycol succinate column were carried out at ca. 200C using nitrogen gas (flow rate 33 ml/min). Those on 20% ethyleneglycol succinate were effected at ca. 170C with nitrogen gas (flow rate 33 ml/min). Gas chromatograms of soybean oil methyl ester, before and after reduction, are shown in Fig. 1.

Isolation of Hydrazones after Hydrogenation

2,4-Dinitrophenylhydrazine (2.0 g), sulfuric acid (30 ml), and ethanol (90%, 30 ml) were diluted with water up to 1 liter. Fifty milliliters of this solution was added to the solvent which was distilled from a reaction mixture after hydrogenation. After several

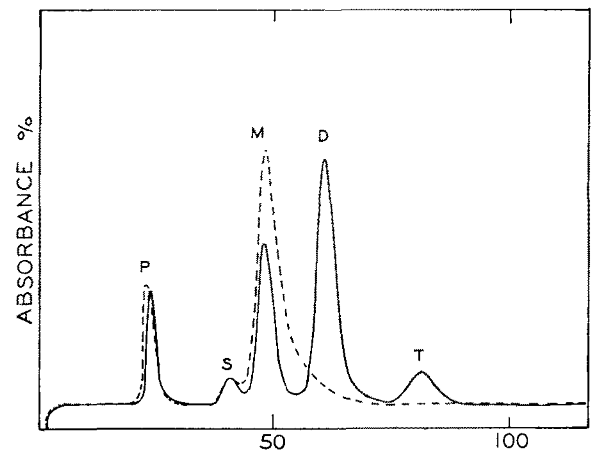

FIG. 1. Gas chromatogram of soybean oil methyl ester from 20% diethyleneglycol succinate at 202C,———; after hydrogenation (Experiment 1)............ P = palmitate, S = stearate, M = monoenoate, D = dienoate, T = trienoate.

TABLE I

Hydrogenation of Soybean Oil Methyl Ester (2.0 g) With Palladium Complexes (0.63 mM) and Salts (4.4 mM) Under *Various Conditions*

Exp.	Catalysts	Solvent[a]	Gas	Atm.	Temp, C	Hr	ppt after[b] hydrogenation	IR Analysis[c] trans %	Column[d]	G-L Analysis[e] P	S	M	D	T or c-t	t-t
1	$(\O_3P)_2PdCl_2 + SnCl_2 \cdot 2H_2O$	ØH-MeOH	H_2	39.1	90	3	+	69.6	d	12.0	4.1	83.9			
2	″ ″ $+ HCl$[g]	″	″	″	″	″	+	65.6	d	10.8	4.4	84.8			
3	$(\O_3P)_2PdCl_2 + SnCl_2 \cdot 2H_2O$	″	″	27.2	″	″	+	69.2	d	12.1	4.3	83.6			
4	″	″	″	13.6	″	″	+	68.7	d	11.8	4.3	83.9			
5	″	″	″	39.1	60	″	—	14.4	d	11.9	4.4	32.2	36.2	7.9	7.3
6	″	″	″	″	″	5	—	19.8	d	11.8	4.4	32.1	32.8	9.1	9.8
7	″	″	″	″	″	12	+	71.6	d	11.9	4.3	83.8			
8	″	″	″	″	40	12	—	14.3	d	11.5	4.5	30.2	39.0	8.0	6.8
9	″	″	″	″	24	3	—	18.2	d	11.0	4.0	28.0	38.4	9.5	9.1
10	″	″	″	″	24	9	—	17.4	d	11.4	4.4	29.2	35.5	8.5	10.0
11	″	Tol-t-BuOH	″	″	60	5	—	36.2	d	11.8	4.5	37.6	24.9	10.7	10.5
12	″ $+ KOH$[f]	ØH-MeOH	″	″	″	5	—	18.3	d	11.7	4.5	32.6	31.9	10.0	9.3
13	$(\O_3P)_2PdCl_2 + SnCl_2 \cdot 2H_2O$	ØH-EtOH	″	″	″	5	—	14.1	d	11.6	4.4	31.5	36.5	8.0	8.0
14	″ 2	ØH-Ac	″	″	″	5	—	13.5	d	11.8	4.4	31.4	34.7	10.3	7.4
15	″	ØH-tBuOH	″	″	″	5	—	4.1	d	11.5	4.4	27.8	48.6	7.7	
16	″	Tol-t-BuOH	″	″	90	3	+	52.6	d	3.5	2.0	26.8			
										7.3 (Bu)[h]	3.9 (Bu)	56.5 (Bu)			
17	″	″	″	1.0	100	3	—	4.5	d	10.5	4.1	25.1	41.5	10.7	8.0
18	″ $+ KOH$[f]	″	″	1.0	100	3	+	5.7	d	11.7	4.3	27.9	41.6	9.0	5.7
19	$(\O_3P)_2PdCl_2$	ØH-MeOH	″	39.1	90	3	—	31.7	d	12.8	5.4	37.0	26.1	6.6	11.1
20	″	″	″	″	″	12	—	53.3	d	11.8	8.2	56.6	16.0	1.8	5.7
21	$(\O_3P)_2PdCl_2 + GeCl_2$	″	″	″	″	3	—	38.8	d	11.6	4.9	50.1	20.2	4.1	10.1
22	$(\O_3P)_2Pd(CN)_2$	″	″	″	″	12	—	63.1	d	11.8	5.4	82.8			
23	″	″	″	″	″	3	—	16.7	e	12.0	4.0	41.7	37.8	4.5	
24	$(\O_3P)_2Pd(CN)_2$	ØH-MeOH	H_2	39.1	70	12	—	50.2	d	10.7	7.3	55.1	26.2	0.7	
25	″	ØH-BuOH	″	″	90	12	—	40.3	d	10.5	6.8	49.8	32.0	0.9	
26	″ $+ SnCl_2 \cdot 2H_2O$	ØH-MeOH	″	″	90	3	—	16.8	d	11.1	4.3	34.1	39.5	6.9	4.1
27	$(\O_3As)_2Pd(CN)_2$	″	″	″	90	12	+	69.0	d	10.6	4.6	38.7	38.0	4.6	3.7
28	″	″	″	″	90	3	+	54.0	d	10.7	4.4	34.8	44.7	3.2	2.2
29	$(\O_3As)_2PdCl_2 + SnCl_2 \cdot 2H_2O$	″	″	″	90	3	+	17.2	e	11.7	3.8	30.6	45.8	8.0	
30	″	″	″	″	60	6	+	7.0	d	11.4	4.4	28.8	45.1	10.3	
31	$(\O_3As)PdCl_2$	″	″	″	90	3	+	13.8	d	11.3	4.3	30.8	46.3	7.3	
32	$K_2PdCl_4 + Sn_2 \cdot 2H_2O$	″	″	″	60	5		0	d	11.1	4.1	27.6	50.0	7.3	
33	Cl ″	″	″	″	90	3	—	0	d	10.4	4.3	28.3	49.3	7.4	
34	$PdCl_2 + SnCl_2 \cdot 2H_2O$	″	″	″	60	3	+	0	e	10.8	3.6	27.0	50.8	7.8	
35	″	″	″	″	90	3	+	0	e	11.3	3.9	27.0	50.1	7.8	
36	$(\O_3P)_2Pd(SCN)_2$	″	″	″	90	3	—	0	e	10.9	3.9	27.0	50.4	7.7	
37	″ $+SnCl_2 \cdot 2H_2O$	″	″	″	90	3	—	0	e	11.3	3.7	26.8	50.9	7.3	
38	$(\O_3P)_2PdCl_2 + SnCl_2 \cdot 2H_2O$	″	N_2	27.2	90	3	+	62.3	d	10.6	4.7	83.2	1.5		
39	$(\O_3P)_2PdCl_2 + GeCl_2$	″	N_2	27.2	90	3	—	23.6	d	12.1	5.7	38.8	32.4	4.4	6.6
40	$(\O_3P)_2Pd(CN)_2$	″	N_2	27.2	90	12	—	44.5	d	10.6	7.7	53.2	27.5	1.0	
Blank[i]								0	d	10.8	4.0	27.3	50.1	7.8	
Blank								0	e	11.0	4.4	27.7	49.3	7.6	

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[a] ØH-MeOH means benzene (30 ml) and methanol (20 ml); t-BuOH means toluene (30 ml) and n-butanol (20 ml); ØH-EtOH means benzene (30 ml) and ethanol (20 ml); ØH-ac means benzene (30 ml) and acetone (20 ml); ØH-tBuOH means benzene (30 ml) and t-butanol (20 ml); ØH-BuOH means benzene (30 ml) and n-butanol (20 ml).

[b] +means that a precipitate was present *after hydrogenation due to the decomposition of catalyst; — means that the solution was homogeneous after hydrogenation.*

[c] % trans isomer as elaidate.

[d] d was carried out on 20% diethyleneglycol succinate; e was carried out on 20% ethyleneglycol succinate.

[e] Abbreviations: S means stearate; P means palmitate; M means monoenates, including oleate; D means dienoates, including linoleate; T or c-t means trienoates, including linolenate and cis, trans conjugated dienoate; t-t means trans, trans conjugated dienoate.

[f] KOH (0.07 g, 1.2 mMol).

[g] HCl (0.7 N, 4 ml, 2.8 mMol).

[h] (Bu) means butyl ester of fatty acid.

[i] Soybean oil methyl ester as starting material.

days, crystals separated. These were recrystallized from ethanol. From the solution from Exp. 16 were obtained crystals having mp 121C. This is identical with that of the derivative of butylaldehyde. In Exp. 6 and 12, the derivative of formaldehyde (mp 165C) was obtained and in Exp. 13, the derivative of ethyl aldehyde (mp 161°).

Results and Discussion

The palladium complexes described in this paper are stable and resemble the analogous platinum complexes in solubility. However, our attempts and those of others to isolate pure hydridopalladium complexes have failed. Only isolation of crude hydride has been reported (15). This is in line with the fact that palladium complexes are generally less stable than the platinum analogues.

Hydrogenations of soybean oil methyl ester were carried out using a variety of palladium complexes under various conditions of temperature, pressure, reaction time and solvent as shown in Table I. The soybean oil methyl ester consisted of 10.8% palmitate, 4.0% stearate, 27.3% oleate, 50.1% linoleate and 7.8% linolenate; the unsaturated components have the *cis* configuration. Methyl oleate was chosen for investigation of the isomerization of a double bond as shown in Table II. The compositions of the hydrogenated esters were determined by infrared and gas-liquid chromatographic analyses. It is seen from Table I that during hydrogenation, the proportion of methyl monoenates increases, the dienoates and trienoates decrease, and in many cases, *trans, trans* and *cis, trans* conjugated dienoates are formed. The content of *trans* isomers (measured as elaidate) increased concurrently, but not regularly, with the increase of the monoenates. It is especially noteworthy that the stearate increased negligibly or not at all.

Hydrogenation and isomerization reactions depend on operating variables such as reaction conditions, solvents and the nature of the catalysts. These effects are discussed in the following sections:

Effect of Varying the Catalysts

Using various catalysts under the same conditions (39.1 atm of hydrogen, 90C, 3 hr) the extent of monoene formation was found to decrease in the following order: $(\phi_3P)_2PdCl_2 + SnCl_2 \cdot 2H_2O > (\phi_3P)_2PdCl_2 + GeCl_2 > (\phi_3P)_2Pd(CN)_2 > (\phi_3P)_2PdCl_2 > (\phi_3As)_2Pd(CN)_2 \gg (\phi_3As)_2PdCl_2$ (Exp. 1, 21, 23, 19, 28 and 31). The $(\phi_3P)_2PdCl_2$-$SnCl_2$ mixture is the most effective catalyst, and converts both linoleate and linolenate to monoenes almost completely but not at all to stearate (Exp. 1). The monoenes obtained under the given conditions are 80.9 to 82.8% of the transconfiguration (Exp. 1, 2, 3, and 4). Hydrogenation with $(\phi_3P)_2Pd(CN)_2$ converts linoleate and linolenate to monoenes only partially in 3 hr (Exp. 23) but almost completely in 12 hr (Exp. 22). On the other hand, neither hydrogenation nor isomerization were observed under the catalytic influence of $PdCl_2 + SnCl_2 \cdot 2H_2O$ or $K_2PdCl_4 + SnCl_2 \cdot 2H_2O$ (Exp. 32 to 35). Addition of tin chloride did not effect catalysis by $(\phi_3P)_2Pd(CN)_2$, $(\phi_3P)_2Pd(SCN)_2$, or $(\phi_3Sb)_2PdCl_2$ (Exp. 26, 37 and 48). Addition of mercuric chloride, which is known to form a chlorine bridged palladium complex (16), is also ineffectual (Exp. 47).

Having considered the effect of varying the catalyst, we shall consider the effect of other variables, using only $(\phi_3P)_2PdCl_2 + nSCl_2 \cdot 2H_2O$ as the catalyst.

Effect of Pressure

No pressure dependence in the degree of hydrogenation was observed in the range of 13.6 atm to 39.1 atm of hydrogen (Exp. 1, 3 and 4). At atmospheric pressure, however, no hydrogenation took place, though there was some isomerization to form conjugated dienes (Exp. 17 and 18). This isomerization may be important in the preparation of drying oils.

Effect of Temperature

Temperature variations were found to be a significant factor in both hydrogenation and isomerization reactions, the proportions of monoenes and trans isomers increasing with increasing temperature. At 90C, hydrogenation was almost complete in 3 hr (Exp. 1, Fig. 1). The reactions at 60C and 24C gave monoenes in low yields but were accompanied by the formation of significant quantities of conjugated dienes (Exp. 5 and 9). It should be noticed, however, that the catalyst decomposed when the reaction was run at 90C, but not when it was run at 60C.

Effect of Solvent

When hydrogenation was carried out in different solvents under fixed conditions, increasing proportions of monoenes and decreasing proportions of dienes were formed in the following order: n-butanol > ethanol, methanol, acetone > t-butanol (Exp. 11, 13, 6, 14 and 15). However, the complex used was sparingly soluble in t-butanol. This order is the same as the tendency of these solvents to deprotonate. That the alcohols were oxidized was shown by the isolation of the 2,4-dinitrophenylhydrazine derivatives. It has been reported (17) that even in the presence of hydrogen under high pressure, the

TABLE II

Hydrogenation[a] of Olefines with Palladium Complexes as Catalysts in a Mixture of Benzene (30 ml) and Methanol (20 ml) at 90C

Exp.	Catalysts	Olefines	Pressure	Conditions		pptn. after[b] hydrogenation	IR Analysis trans %[c]	GL[d] Analysis		
				Atm.	Hrs.			Stearate	Monoenate	Dienoate
41	$(\varnothing_3P)_2PdCl_2 + SnCl_2 \cdot 2H_2O$	Oleate	N_2	27.2	3	+	13.2		100	
42	$(\varnothing_3P)_2PdCl_2 + GeCl_2$	Oleate	N_2	27.2	3	—	0		100	
43	$(\varnothing_3P)_2Pd(CN)_2$	Oleate	N_2	27.2	12	—	2.8		100	
44	$(\varnothing_3P)_2PdCl_2 + SnCl_2 \cdot 2H_2O$	Oleate	H_2	39.1	3	+	74.6		100	
45	$(\varnothing_3P)_2PdCl_2 + GeCl_2$	Oleate	H_2	39.1	3	—	70.6		100	
46	$(\varnothing_3P)_2Pd(CN)_2$	Oleate	H_2	39.1	12	—	56.5	2.3	95.0	2.7
47	$(\varnothing_3P)_2PdCl_2 + HgCl_2$	Linoleate	H_2	39.1	5	+	11.7		0.3	99.7
48	$(\varnothing_3Sb)_2PdCl_2 + SnCl_2 \cdot 2H_2O$	Linoleate	H_2	39.1	5	+	3.3			100

[a] Methyl oleate (1.5 g, 4.1 mMol) was treated with the palladium complex (0.63 bMol) and tin (II) chloride or germanium (II) chloride (4.4 mMol). Methyl linoleate 3.4 mMol) was treated with palladium complex (0.34 mMol) and tin (II) dichloride (1.7 mMol).

[b] + means precipitation after hydrogenation.
— means no precipitation after hydrogenation.

[c] % trans isomer as elaidate.

[d] GL chromatography was carried out using 20% diethyleneglycol succinate as shown in the Experiment section.

formation of hydrido platinum complexes in alkaline alcoholic solution is accompanied by the formation of aldehyde.

Ester Exchange Reaction

In a mixture of n-butanol and toluene, hydrogenation was accompanied by ester exchange (Exp. 16). IR analysis indicated that the resulting ester contained 52.6% trans isomers and no conjugated dienes. Chromatographic analysis showed the following composition: 3.5% methyl palmitate, 9.3% mixed methyl stearate and butyl palmitate, 26.8% methyl monoenes, 3.9% butyl stearate and 56.5% butyl monoenes. Assuming that the hydrogenated ester contained 10.8% palmitate, the same as that of the original ester, the ratio of butyl ester to methyl ester is 2:1 in palmitate, 2:0 in stearate and 2:1 in monoenes. This suggests that the conversion of methyl ester to butyl ester takes place in the ratio of 1:2. On the other hand, no ester exchange reaction was obsrved at 60C (Exp. 11).

Effect of Acid and Base

Addition of acid and base was found to have no effect on either hydrogenation or isomerization (Exp. 2, 12 and 18).

Catalytic Effect of Dicyano-Bistriphenylphosphine-Palladium (II)

This complex is effective for hydrogenation and isomerization reactions without the addition of tin (II) chloride. Under its influence, soybean oil methyl ester was only partially reduced after 3 hr but almost completely after 12 hr (Exp. 23 and 22). The extent of hydrogenation depends remarkably upon the temperature (Exp. 22 and 24). The cyano triphenylphosphine complex is a more effective catalyst than the cyano triphenylarsine (Exp. 22 and 27). The ester exchange reaction was not observed in the presence of this catalyst (Exp. 25).

Reaction of Oleate

Under either nitrogen or hydrogen, in a mixture of benzene and methanol, oleate was converted to the *trans* isomers but not at all to stearate. However, the isomerization reaction is remarkably slower under nitrogen pressure than under hydrogen pressure (Exp. 41 and 46).

Hydrogenation of Soybean Oil Methyl Ester Under Nitrogen Pressure

Under nitrogen pressure, hydrogenation and isomerization reactions were observed to proceed effectively in mixtures of benzene and methanol (Exp. 38, 39 and 40). Nevertheless, the isomerization of olefine under the same conditions was shown to be remarkable slow (Exp. 41, 42 and 43).

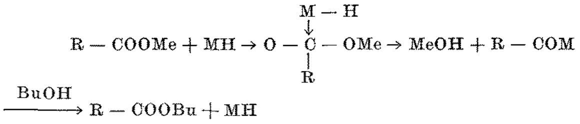
Catalytic hydrogenation and isomerization of these esters with palladium complexes is believed to follow a path similar to that observed with the mixture of $(\emptyset_3P)_2PtCl_2$ and $SnCl_2 \cdot 2H_2O$ (7). However, neither the palladium hydride nor a reaction intermediate was isolated. The catalytic effect is sensitive to the nature of the ligands on the metal ion and to the addition of salts such as $SnCl_2$ and $GeCl_2$. It is remarkable that catalysis takes place under nitrogen pressure but in the absence of hydrogen. Formation of the hydrido complex seems to be the first step in the reaction:

$$\begin{matrix} L_2PdCl_2 + SnCl_2 \\ \text{or} \\ L_2Pd(CN)_2 \end{matrix} \xrightarrow{H_2 \text{ or } CH_3OH} MH + HCHO \quad \begin{pmatrix} M = \text{Pd complex} \\ L = \emptyset_3P \text{ or } \emptyset_3As \end{pmatrix}$$

Isomerization of the double bonds then results from addition and elimination reactions.

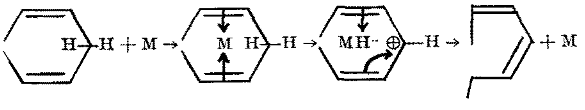
The mechanism of hydrogenation reactions catalyzed by iridium and rhodium complexes has been discussed recently (18). Although palladium complexes are quite different in their catalytic activities from the iridium and rhodium complexes, their reactions can be explained by assuming that the hydride complex is activated due to expansion of the coordination sphere of the metal ion and a decrease in the formal charge on the complex (19).

That ester exchange was noted in n-butanol solution under the influence of $(\emptyset_3P)_2PdCl_2 + SnCl_2$ but not with $(\emptyset_3P)_2Pd(CN)_2$ may be due to the formation of an acyl complex accompanied by direct alcoholysis (20):



$$R-COOMe + MH \rightarrow O-\underset{\displaystyle R}{\underset{|}{\overset{\overset{\displaystyle M-H}{\downarrow}}{C}}}-OMe \rightarrow MeOH + R-COM$$
$$\xrightarrow{BuOH} R-COOBu + MH$$

Under nitrogen pressure, isomerization and hydrogenation of linoleate are faster than isomerization of oleate (Exp. 38 and 41). This suggests that catalysis under nitrogen pressure proceeds in a different way than under hydrogen pressure. The palladium complex may be activated by being coordinated to two double bonds. Subsequently, a hydride shift from substrate to metal ion causes concerted migration of a double bond to form a conjugated diene:



This hydride shift is confirmed by the fact that oleate was converted partially to dienes and stearate during hydrogenation (Exp. 46).

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[Received August 15, 1966]