Catalytic Hydrogenation of Soybean Oil Methyl Esters and Some Related Compounds

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Abstract

Mixtures of platinum complexes and tin(II) chloride are effective homogeneous catalysts for the hydrogenation of soybean oil methyl ester, reducing it to the monoene stage only. Hydrogenation and isomerization reactions have been examined under various conditions, using a solvent consisting of 60% benzene and 40% methanol.

The extent of hydrogenation depends upon the temperature (90C > 60C > 30C) but not upon the pressure (1075 psi as compared with 525 psi). It almost stops after 3 hr, although one double bond remains in the molecule.

After hydrogenation with a catalyst consisting of a mixture of dichloro-*bis*-triphenylphosphine-platinum(II) and tin(II) chloride, soybean oil methyl ester shows an increase in monoene, a decrease in diene and triene, and formation of conjugated *cis-trans* and *trans-trans* dienes, but no increase in stearate. Similarly, methyl oleate and methyl linoleate were converted to trans monoene, but not to stearate.

Hydrogenations with mixtures of tetrachloro-platinum(II) ion or hexachloro-platinum(IV) ion and tin(II) chloride were similar to those described above but they form some stearate.

Several other metal ions were studied as replacements for tin. None of them were effective.

Introduction

There has been a good deal of interest in homogeneous hydrogenation in recent years. The subject is important because, from a theoretical point of view, its study throws light upon the mechanism of reactions, and upon the nature of heterogenous catalysis, and from a practical point of view, because homogeneous catalysts may show a higher activity and selectivity than the hetergeneous catalysts that have commonly been used.

A variety of metal ions and complexes has been shown to activate molecular hydrogen in solution. These have been reviewed by Halpern (1). Olefinic compounds have been successfully hydrogenated under homogeneous conditions under catalytic influence of pentacyano-cobaltate(II) ion (2), metal carbonyls (3), ruthenium(II) ion (4), hydrocarbon soluble Ziegler type catalysts (5), and platinum(II)-tin (II) catalysts (6). Transition metal complexes, in general, have the ability to form hydride complexes (7) and π-complexes with olefinic compounds (8).

In beginning this study of the homogeneous hydrogenation of soybean oil methyl ester, we were encouraged by reports of successful experiments in which pentacyano-cobaltate(II) ion (9) and iron pentacarbonyl (10) had been used as catalysts.

Cramer et al. (6) have reported the homogeneous hydrogenation of ethylene by a platinum(II) chloride-tin(II) chloride complex. We have found that platinum(II)-tin(II) complexes do not catalyze the hydrogenation of soybean oil methyl ester at atmospheric pressure, but do so effectively under high pressure of hydrogen. This report describes the use of these catalysts in the hydrogenation of soybean oil methyl ester and methyl linoleate.

Experimental

Materials

One liter of commercial soybean oil was purified by shaking it with 200 ml of 5% aqueous sodium hydroxide. The mixture was allowed to stand for 2 hr before the aqueous layer was removed. The oil which remained was washed again with 5% aqueous sodium hydroxide, washed twice with water, twice with a saturated aqueous solution of potassium chloride, and then extracted with two liters of diethyl ether. The extract was washed with water, and finally dried over calcium chloride. The ethereal solution was heated on a steam bath under diminished pressure to remove the ether. For the purified oil, $N_D^{25} = 1.4722$; iodine value = 129.4 (measured by Hanus method) (11).

The formation of the methyl ester of soybean oil was effected as described by Hartman (12). The methyl ester which boiled in the range 166C–184C at 1.5 mm Hg was collected. $N_D^{25} = 1.4543$; iodine value by Hanus method, 128.2.

Methyl oleate and linoleic acid were obtained from Hormel Institute, University of Minnesota, Austin, Minn.

For the preparation of methyl linoleate, a mixture of 23 g of linoleic acid, 4 ml of sulfuric acid, and 150 ml of anhydrous methanol was refluxed for 2½ hr. The acid was neutralized by the addition of anhydrous sodium carbonate, and the methanol was removed by distillation. The residue was diluted with 200 ml of diethyl ether, and the solution was washed twice with 10% sodium carbonate solution and twice with water. After drying over anhydrous magnesium sulfate, the solution was concentrated and the methyl linoleate was distilled at 154–155C/1.5 mm Hg.

Dichloro-*bis*-triphenylphosphine-platinum(II), $[(C_6H_5)_3P]_2PtCl_2$, was prepared from K_2PtCl_4 (13) and triphenylphosphine by the procedure described in the literature (14). After one recrystallization from chloroform and n-heptane, this substance melted at 312C (dec.). It is soluble in chloroform and dimethylformamide, but insoluble in water, methanol, ethanol, benzene, acetone, methyl acetate, and diethyl ether.

The methanol solution of dry hydrogen chloride

TABLE I

Hydrogenation of Soybean Oil Methyl Ester (Exp. 1–18) Methyl Oleate (Exp. 19 and 20) and Methyl Linoleate (Exp. 21 and 22)

Exp.	Catalysts	Conditions			I.V.[a]	Total[b] *trans* (%)	Compositions (%)[c]							*trans* monoene
		Temp, C	psi of H_2	hr			Palmitate	Stearate	Monoene	Diene[i]	Triene or *c-t*-conj-diene[d]	*t-t*-conj-diene[e]	Column	
Control[f]					125.0 125.0	0 0	10.9 11.0	3.8 4.0	28.3 27.2	50.5 49.1	6.5 8.7	no no	a[g] b[h]	no
1	$(\O_3P)_2PtCl_2$ 0.50 g	90	575	3	116.4	4.4	11.1	4.1	30.2	48.8	5.8	no	a	
2	$SnCl_2 \cdot 2H_2O$ 1.08 g	90	575	3	123.6	0.0	11.6	4.5	27.9	47.7	8.3	no	b	
3	$(\O_3P)_2PtCl_2 + SnCl_2 \cdot 2H_2O$ 0.50 g 1.08 g	90	575	3	78.1	77.4	11.8	4.4	78.5	5.4	no	no	b	
4		90	1075	3	81.1	73.7	12.9	4.2	79.5	3.4	no	no	b	
5		90	575	11	75.7	69.6	11.5	4.4	84.1	no	no	no	a	82.7
6	$(\O_3P)_2PtCl_2 + SnCl_2 \cdot 2H_2O + HCl$ in CH_3OH 0.50 g 1.08 g 0.715 N, 1.87 ml	60	550	3	93.0	57.2	12.0	4.2	34.5	22.1	14.5	12.7	a	
7	$(\O_3P)_2PtCl_2 + SnCl_2 \cdot 2H_2O$ 0.50 g 1.08 g	60	550	19	87.5	51.7	11.7	4.3	63.3	11.7	3.0	6.0	a	
8		30	525	3	99.3	38.7	11.7	4.8	30.0	23.8	17.9	11.8	b	
9	$(\O_3P)_2PtCl_2$ 0.20 g	60	550	3	117.7	3.6	11.8	4.1	27.8	47.5	8.4	no	b	
10	$(\O_3P)_2PtCl_2 + SnCl_2 \cdot 2H_2O$ 0.20 g 0.43 g	60	550	3	101.1	33.0	11.6	4.3	33.4	30.0	14.5	6.2	a	
11	$(\O_3P)_2PtCl_2 + SnCl_2 \cdot 2H_2O$ 0.20 g 0.17 g	60	550	3	112.3	16.8	11.5	4.0	30.2	38.4	11.7	4.2	a	
12	$(\O_3P)_2PtCl_2 + SbCl_3 + HCl$ in CH_3OH 0.20 g 0.81 g 0.715 N, 1.87 ml	60	550	4	120.6	0.8	11.5	4.1	28.3	49.7	6.4	no	a	
13	$(\O_3P)_2PtCl_2 + AlCl_3$ 0.20 g 0.245 g	60	550	3	121.1	0.0	10.9	4.2	28.6	50.0	6.3	no	a	
14	$(\O_3P)_2PtCl_2 + Hg(OAc)_2 + HCl$ in CH_3OH 0.20 g 0.245 g 0.715 N, 1.87 ml	60	550	3	119.6	1.1	11.3	3.7	28.3	50.7	6.0	no	a	
15	$(\O_3P)_2PtCl_2 + Ni(acac)_2 + HCl$ in CH_3OH 0.20 g 0.19 g 0.715 N, 1.87 ml	60	550	3	119.0	1.2	11.6	3.8	29.9	48.9	5.8	no	a	
16	$H_2PtCl_2 + SnCl_2 \cdot 2H_2O + HCl$ in CH_3OH 0.209 g 1.08 g 0.715 N, 1.87 ml	90	590	3	49.0	46.5	11.0	31.4	57.6	no	no	no	a	80.7
17	$H_2PtCl_6 + SnCl_2 \cdot 2H_2O$ 0.209 g 1.08 g	90	575	3	49.2	46.6	10.9	31.1	58.1	no	no	no	a	80.2
18	$K_2PtCl_4 + SnCl_2 \cdot 2H_2O + HCl$ in CH_3OH 0.246 g 1.08 g 0.715 N, 1.87 ml	90	580	3	67.9	63.7	12.5	8.8	78.5	no	no	no	b	81.2
19	Oleate + $(\O_3P)_2PtCl_2 + SnCl_2 \cdot 2H_2O$ 2.0 g 0.50 g 1.08 g	90	575	3	81.5	81.7	no	no	100	no	no	no	a	81.7
20	Oleate + $H_2PtCl_6 + SnCl_2 \cdot 2H_2O$ 2.0 g 0.209 g 1.08 g	90	575	3	45.5	44.0	no	45.5	54.5	no	no	no	a	80.8
21	Linoleate + $(\O_3P)_2PtCl_2 + SnCl_2 \cdot 2H_2O$ 2.5 g 0.50 g 1.08 g	90	575	3	107.1	65.4	no	no	29.9	29.6	13.7	26.6	b	
22	Linoleate + $H_2PtCl_6 + SnCl_2 \cdot 2H_2O + HCl$ in CH_3OH 2.5 g 0.209 g 1.08 g 0.715 N, 1.87 ml	90	575	3	62.5	54.5	no	no	26.0	74.0	no	no	b	

[a] Iodine values by Hanus method.

[b] The *trans* content was calculated as elaidate by infrared spectroscopy.

[c] Compositions were determined by gas chromatography.

[d] *c-t*-conj-diene means *cis-trans* conjugated diene.

[e] *t-t*-conj-diene means *trans-trans* conjugated diene.

[f] Soybean oil methyl ester as starting material.

[g] Conditions: 20% diethyleneglycol succinate on Chromosorb W 60–80 mesh, 10 ft x ⅛ in. copper column, temperature 205C, flow 30 ml/min N_2, using Hi-Fy flame ionization detector.

[h] Conditions: 20% diethyleneglycol succinate on Chromosorb W 60–80 mesh, 10 ft x ⅛ in. glass column, temperature 200C, flow 30 ml/min N_2, using Hi-Fy flame ionization detector.

[i] "Diene" refers to nonconjugated diene.

(0.715 N) was prepared by bubbling dry HCl gas through sulfuric acid and then into anhydrous methanol. The normality was determined by titration with 1N NaOH using phenolphthalein as the indicator.

Hydrogenation with Platinum(II)-Tin(II) Complexes

The reaction mixture in Experiments 1–18 consisted of 2.0 g of soybean oil methyl ester, and the catalyst (Table I), dissolved in a mixture of benzene (30 ml) and methanol (20 ml). In Experiments 19 and 20, methyl oleate (I.V., 81.5) was substituted for the soybean oil methyl ester, and in Experiments 21 and 22, 2.5 g of methyl linoleate (I.V., 167.1) was used.

The hydrogenation reactions were carried out in a glass bottle which was contained in a stainless steel autoclave of 120 ml capacity. The autoclave containing the reaction mixture was evacuated, flushed with hydrogen four times, and then pressured with hydrogen to 500 psi at room temperature.

After hydrogenation, the solution was evaporated on a steam bath, and the residue was treated with 15 ml of 10% aqueous sodium carbonate solution. In each experiment, a precipitate formed. The solution containing the precipitate was shaken with 100 ml of diethyl ether, after which the precipitate was removed. The solution was washed with water. The ether was evaporated, and the reduced ester was distilled at a pressure of 1.5 mm Hg. In most cases, the yield exceeded 1.5 g. The hydrogenated products were analyzed by means of gas chromatography and infrared spectroscopy, and the iodine value was measured.

Analysis by Infrared Spectroscopy

The infrared absorption of the esters containing isolated double bonds was measured by a standard method (15) on a Beckman IR5A spectrophotometer, using a 1 mm potassium bromide cell. The amount of *trans* double bond contained in the hydrogenated esters was calculated using methyl elaidate as a standard. The mean error in the absorbance curve for the primary standard was ±1.6%.

The reduced ester from Experiment 5 did not show the presence of conjugated diene. There was only a single peak in the infrared spectrum in the 10–11 μ region (Fig. 1). However, the sample from Experiment 6 showed intense absorption bands at 10.55, 10.13, and 10.34 μ, characteristic of conjugated *cis-trans* diene and *trans* monoene (Fig. 2). The nature of the *cis-trans* diene was not determined from the infrared spectrum.

FIG. I

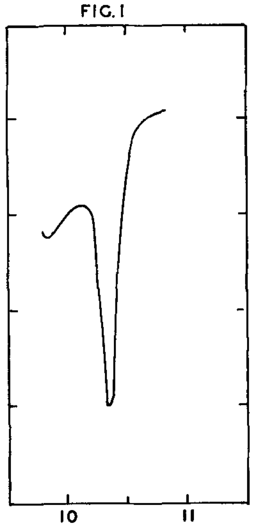

FIG. 2

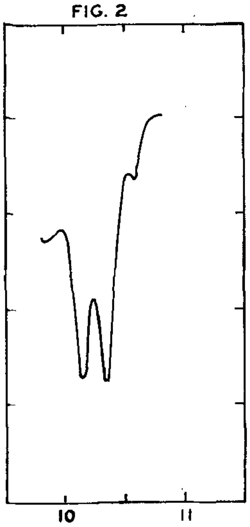

FIG. 1. Infrared spectrum of reduced soybean oil methyl ester (Exp. 5, Table I).

FIG. 2. Infrared spectrum of reduced soybean oil methyl ester (Exp. 6, Table I).

Determination of Iodine Values

Iodine values of the starting material and the hydrogenated ester were determined by Hanus method (11).

Analysis by Gas Chromatography

Analyses by gas chromatography were carried out with a Hy-Fi flame ionization Aerograph and a 10 ft x $\frac{1}{8}$ in. copper column packed with Chromosorb W, 60–80 mesh, coated with 20% diethylene-glycol succinate at 205C with a nitrogen flow rate of 30 ml/min.

Results

By using mixtures of either dichloro-*bis*-triphenylphosphine-platinum(II) or chloroplatinic acid with tin(II) chloride dihydrate as catalysts, soybean oil methyl ester and methyl linoleate were hydrogenated effectively and specifically.

Allen (16) reported the selective hydrogenation of soybean oil, using nickel as a heterogeneous catalyst at 285F and 30 psi of hydrogen. The hydrogenated oil had the following acid composition: palmitic, 11.8%; stearic, 5.7%; oleic, 61.5%; linoleic, 20.1%; linolenic, 1.0%; *trans* double bond, 36.1%.

Zajcew (17) reported the heterogeneous hydrogenation of soybean oil, using a palladium catalyst at 114C and 47 psi of hydrogen for 70 min. The product contained linoleic acid, 11.3%, saturated compounds. 19.1%, and *trans* compounds, 35%.

Frankel et al. (10) have reported the homogeneous hydrogenation of soybean oil methyl ester, using iron pentacarbonyl at 180C and 310 psi of hydrogen for 1 hr. The original ester contained palmitate, 10.4%; stearate, 3.7%; oleate, 26.7%; linoleate, 50.4%; and linolenate, 9.5%. In the reduced ester, the triene was decreased by 9.5% and the diene by 19.2%, while the monoene plus stearate was increased by 18.4%, the conjugated diene by 7.7%, and the *trans* double bond (as elaidate), by 16.6%.

In a typical experiment in this study (Exp. 3), the reduction product of soybean oil methyl ester showed the following composition: palmitate, 11.8%; stearate 4.4%; monoene, 78.5%; diene, 5.4%; *trans* double bond (as elaidate), 78.1%. In this experiment, linoleate and linolenate were almost completely converted to monoene, and oleate was not reduced at all. The infrared spectrum of the reduced esters showed them to be largely in the *trans* configuration.

The platinum-tin complex is remarkable in being a more selective catalyst than nickel, palladium, or iron carbonyl. Table I gives data for the hydrogenation of soybean oil methyl ester under various conditions. Hydrogenation and isomerization were not effected by either dichloro-*bis*-triphenylphosphine-platinum(II) or tin(II) chloride alone, as shown in Experiments 1, 2 and 9, but a mixture of the two proved to be an active catalyst, as shown in Experiments 3 to 8 and 10. The dependence of the extent of hydrogenation on temperature is shown by Experiments 3, 6, and 8, in which both triene and diene were changed to monoene; the configuration of the latter changed from *cis* to *trans*. However, at 30C and 60C, these changes were not complete. The hydrogenated esters which were obtained contained *cis-trans* and *trans-trans* conjugated dienes. On the other hand, the extent of hydrogenation does not depend upon the pressure (1075 psi and 575 psi) as shown in Experiments 3 and 4. It seems to proceed rapidly for 3 hr (Exp. 3), and the product is almost completely changed to monoene after 11 hr (Exp. 5). The extent of hydrogenation depends upon the concentration of the complex, and is decreased by decreasing the amount of tin(II) chloride (Exp. 6, 10, and 11).

It is seen from Experiments 16, 17, and 18 that increase of stearate was observed when mixtures of chloroplatinic acid or potassium tetrachloroplatinate (II) and tin(II) chloride were used. Under the conditions of our experiments, these are less selective catalysts than the mixtures of dichloro-*bis*-triphenylphosphine-platinum(II) and tin(II) chloride.

Experiments on the catalytic hydrogenation of methyl oleate and methyl linoleate are also outlined in Table I (Experiments 19–22, inclusive). Examination of these substances was undertaken in the hope that it would give information on the reactivity and isomerization of the double bonds. Under the influence of the phosphine-platinum complex (Exp. 19), methyl oleate was not hydrogenated, but was converted from the *cis* to the *trans* configuration. On the other hand, under the same conditions, the use of chloroplatinic acid as a catalyst effected the formation of the saturated compound, stearate (Exp. 20). It is interesting that in the hydrogenation of methyl linoleate (Exp. 21 and 22), the total *trans* material was obtained in roughly twice as great a yield as the reduction product, monoene.

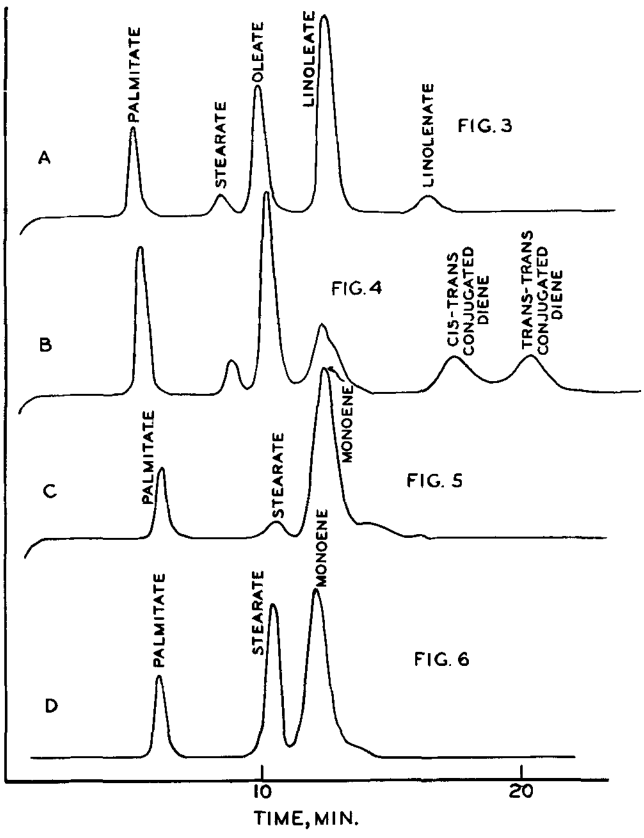

FIG. 3–6. Gas chromatograms of soybean methyl ester and hydrogenated soybean oil methyl ester. Fig. 3, soybean oil methyl ester at 206C; Fig. 4, hydrogenated soybean oil methyl ester at 205C (Exp. 6). Fig. 5, hydrogenated soybean oil methyl ester at 200C (Exp. 5). Fig. 6, hydrogenated soybean oil methyl ester at 200C (Exp. 17).

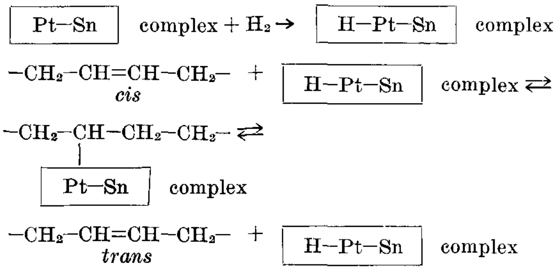

FIG. 7.

The data in Table I show that the platinum complex is not activated by using antimony(III) chloride, aluminum chloride, nickel acetylacetonate, or mercury(II) acetate in place of tin(II) chloride.

Discussion

From the experimental results reported here, a possible mechanism for homogeneous hydrogenation with the catalytic mixture of platinum complexes and tin(II) chloride may be suggested. The exact structure of the platinum-tin complex has not yet been elucidated, but Cramer et al. (6) have reported the isolation of $[\text{Ø}_3PCH_3]_3[Pt(SnCl_3)_5]$. Their x-ray studies have shown that in this 1:5 complex, the tin atoms are arranged around the platinum atom at the corners of a triangular bipyramid, and are attached directly to it. They showed that by addition of tin(II) chloride, platinum(II) chloride was converted to an active catalyst. In the course of our work, we have isolated 1:1 complexes of the type $[(\text{Ø}_3P)_2PtH(SnCl_3)]$, which is effective in the hydrogenation of methyl linoleate (18). The tin chloride-phosphine-platinum complex is not effective in the hydrogenation of isolated double bonds, whereas, under the experimental conditions described in this paper, the tin chloride-chloroplatinic acid mixture brought about partial hydrogenation of such bonds to single bonds. With either type of catalyst, oleate was observed to undergo extensive *cis-trans* isomerization.

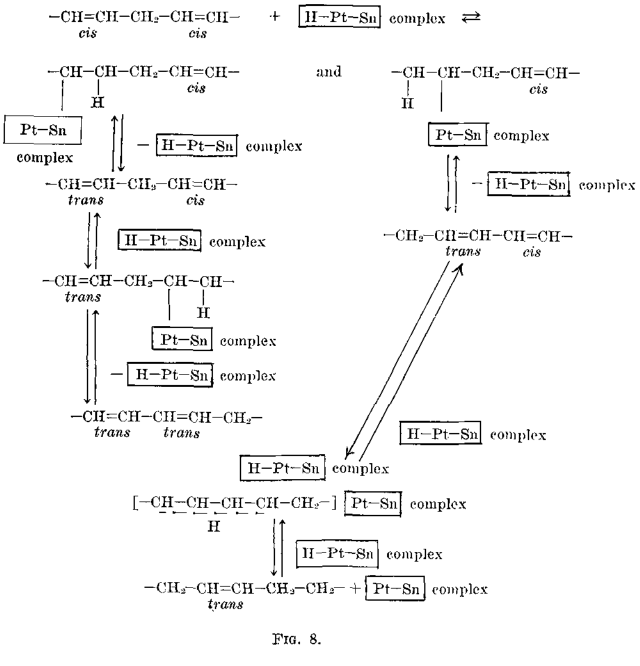

FIG. 8.

Cis-trans isomerization of the double bond was observed in the case of oleate, as shown in Figure 7. The mixture of phosphine-platinum complex and tin(II) chloride was not effective in the hydrogenation of isolated double bonds. However, the mixture of chloroplatinic acid and tin (II) chloride brought about partial hydrogenation of isolated double bonds to single bonds.

Hydrogenation of diene to monoene seems to take place after the nonconjugated diene is converted to conjugated diene, because the "hydrogenation" of nonconjugated diene under mild conditions leads to the formation of *cis-trans* and *trans-trans* conjugated dienes. It is suggested that the nonconjugated diene combines with the platinum-tin catalyst to form a platinum-tin-diene adduct, followed by dehydrogenation with rearrangement to the conjugated diene. Finally, hydrogenation of the conjugated diene takes place by addition of the hydrido-platinum-tin-complex Figure 8.

Soybean oil methyl ester and methyl linoleate were stereospecifically hydrogenated with the mixture of dichloro-*bis*-triphenylphosphine-platinum(II) and tin(II) chloride to form *trans* monoene—not to the saturated compound, stearate. However, with the mixture of chloroplatinic acid and tin(II) chloride, some stearate was formed (Exp. 16 and 17). The great extent of *trans* monoene formation is particularly noteworthy. Oleate was converted to the *trans* configuration to the extent of 81.7% with the phosphine-platinum complex (Exp. 19) and 80.8% with the chloroplatinic acid complex (Exp. 20). On the other hand, soybean oil methyl ester was converted to the *trans* configuration to the extent of 82.7% with the phosphine-platinum complex (Exp. 5), and 80.7% with the chloroplatinic acid complex (Exp. 16). From these results, it may be reasoned that isomerization takes place through the addition of a hydride complex to the double bond rather than through a simple one step transfer of molecular hydrogen from the catalyst to the double bond. An excess of tin(II) chloride was used to facilitate the formation of the platinum-tin complex.

In conclusion, it may be pointed out that homogeneous hydrogenation with platinum-tin complexes is similar in some respects to hydrogenation with pentacyanocobaltate(II) *ion* (2,9) or Ziegler-type soluble catalysts (5). Of course, these tentative suggestions must be reexamined after further experimentation.

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