Homogeneous Catalysis in the Reactions of Olefinic Substances.[1a] VII. Hydrogenation and Isomerization of Methyl Linoleate with Bis(triphenylphosphine)nickel Halides[1b]

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Abstract: Isomerization and selective hydrogenation of methyl linoleate in benzene or tetrahydrofuran are effected by bis(triphenylphosphine)nickel halides in the absence of hydrogen under nitrogen pressure (to maintain comparable conditions) just as they are under hydrogen pressure, though to a lesser extent. The catalytic effects of bis(triphenylphosphine)nickel halides parallel the order of decreasing electronegativity of the halide ions: $Cl^- > Br^- > I^-$. Hydrogenation under hydrogen pressure proceeds more rapidly in benzene solution than in tetrahydrofuran solution. However, hydrogenation in the absence of hydrogen proceeds more rapidly in THF than in benzene. Methyl oleate is converted to *trans* isomers but not to stearate under hydrogen pressure using these catalysts. However, methyl oleate is not affected in the absence of hydrogen. Isomerization of oleate is slower than hydrogenation and isomerization of linoleate.

Selective homogeneous hydrogenations of soybean oil methyl ester and some related compounds have been carried out using platinum[1a,2a] and palladium complexes[2b] as catalysts. Some characteristic features of these catalytic reactions are (1) migration of the double bond, (2) *cis–trans* isomerization of double bonds, (3) selective hydrogenation of polyunsaturated compounds to monounsaturated compounds, (4) transesterification of the methyl ester to the butyl ester, (5) abstraction of hydrogen from the solvents by the metal complexes.

The present report deals with hydrogenation and isomerization reactions of methyl linoleate and methyl oleate using bis(triphenylphosphine)nickel halides as catalysts under various conditions. Bis(triphenylphosphine)nickel halides of tetrahedral configuration have been investigated by X-ray diffraction[3] and measurements of absorption spectra,[4] magnetic moment,[5,6] and dipole moment.[5,6] Bis(triphenylphosphine)nickel complexes are known to be effective catalysts for carbonylation reactions[7–9] and polymerization of acetylene derivatives.[10,11]

Experimental Section

1. Preparation of Dichlorobis(triphenylphosphine)nickel(II), $NiCl_2[(C_6H_5)_3P]_2$.[6,6] A solution of triphenylphosphine (5.0 g) in ethanol (40 ml) was added dropwise with constant stirring to a solution of nickel(II) chloride hexahydrate (2.5 g) in ethanol (30 ml). Crystals separated immediately, but the solution containing the crystals was refluxed for 0.5 hr. After cooling to room temperature, the purple crystals were filtered off and washed with diethyl ether, yield 3.3 g.

Anal. Calcd for $C_{36}H_{30}P_2Cl_2N_2$: C, 66.09; H, 4.26; Cl, 10.80; Ni, 8.97. Found: C, 65.92; H, 4.52; Cl, 10.66; Ni, 8.86.

2. Preparation of Dibromobis(triphenylphosphine)nickel(II), $NiBr_2[(C_6H_5)_3P]_2$.[6,9] **a.** A mixture of anhydrous nickel(II) bromide (2.0 g) and triphenylphosphine (4.8 g) in 1-butanol (40 ml) was refluxed for 2 hr. The solution was filtered while it was still hot. After standing at room temperature, it yielded green crystals which were filtered and washed with diethyl ether, yield 0.8 g. These crystals were recrystallized from a mixture of benzene and *n*-hexane.

Anal. Calcd for $C_{36}H_{30}P_2Br_2Ni$: C, 58.18; H, 4.07; Ni, 7.90. Found: C, 58.29; H, 4.04; Ni, 7.80.

b. A solution of tetrahydrofuran (150 ml) containing triphenylphosphine (10 g) and anhydrous nickel bromide (412 g) was refluxed for 5 hr and then cooled to room temperature. After addition of diethyl ether (150 ml), the solution was left in the refrigerator overnight. The dark green massive crystals which separated were filtered and washed with diethyl ether, yield 9.1 g.

3. Diiodobis(triphenylphosphine)nickel(II) and Dithiocyanatobis(triphenylphosphine)nickel(II). The preparations were carried out as described in the literature.[6]

4. Hydrogenation and Isomerization Reactions of Methyl Linoleate and Methyl Oleate with Nickel Complexes. The hydrogenations of methyl linoleate (1.0 g, 3.4 mmoles) and methyl oleate (1.0 g, 3.4 mmoles) were carried out in a rocking autoclave which contained a glass bottle of 120-ml capacity as already reported.[2a] The nickel complexes (0.68 mmole) or mixtures of them (0.69 mmole) with anhydrous tin(II) chloride (1.7 mmoles) were used as catalysts under various conditions. In these experiments, 1 hr was required to elevate the temperature of the reaction mixture to 90° from room temperature rather than the 15 min required in our earlier experiments.[1a] After reaching the operating temperature, the autoclave was vibrated.

5. Analysis of the Reaction Products. The compositions and structures of the resulting esters were determined by gas chromatography and by infrared spectroscopy as shown in the previous report.[1a]

Results

1. Influence of Different Halide Ions. Bis(triphenylphosphine)nickel halides were observed to be effective in both hydrogenation and isomerization of methyl linoleate to give the isomerized *trans* monoene but not the saturated compound, stearate. Hydrogenation of methyl linoleate under 39.1 atm of hydrogen at 90° for 3 hr showed that the catalytic effectiveness of the nickel complexes parallels the decreasing electronegativity of halide ions ($Cl^- > Br^- > I^-$). The

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Table I. Reactions of Methyl Linoleate (1.0 g, 3.4 mmoles) or Methyl Oleate (1.0 g, 3.4 mmoles) with Bis(triphenylphosphine)nickel Halide (0.64 mmole)

			Conditions				Infrared analysis,	Glpc analysis					
Expt	Catalyst[a]	Substrate[b]	Pressure[c]	Temp, °C	Time, hr	Solvent[d]	*trans* %[e]	U[f]	S[g]	M[h]	D[i]	c–t[j]	t–t[k]
1	RI_2	L	H_2	90	3	C_6H_6	84.7		1.1	83.5	15.4		
2	RI_2	L	H_2	90	3	THF	58.5			83.2	16.8		
3	RI_2	L	H_2	140	3	Tol	65.4		2.0	88.8	9.2		
4	RI_2	L	N_2	90	3	C_6H_6	24.6			25.6	60.4	9.2	4.8
5	RI_2	L	N_2	90	3	THF	43.7		1.4	55.3	39.1	2.0	2.2
6	RI_2	Ol	H_2	90	3	C_6H_6	55.2			100			
7	RI_2	Ol	H_2	90	3	THF	29.0			100			
8	RI_2	Ol	N_2	90	3	C_6H_6	0			100			
9	RI_2	Ol	N_2	90	3	THF	0			100			
10	RBr_2	L	H_2	90	3	C_6H_6	40.9	2.1	3.1	53.0	40.0	1.8	
11	RBr_2	L	H_2	90	3	THF	37.5	1.3	3.1	38.7	48.7	3.3	4.9
12	RBr_2	L	H_2	140	3	Tol	50.5	1.6	5.1	73.2	20.1		
13	RBr_2	L	H_2	90	12	C_6H_6	57.0	2.2	5.8	80.5	11.5		
14	RBr_2	L	N_2	90	12	C_6H_6	23.9		1.6	22.4	69.2	4.0	2.8
15	RBr_2	Ol	H_2	90	12	C_6H_6	58.2			100			
16	RBr_2	Ol	N_2	90	12	C_6H_6	0			100			
17	RCl_2	L	H_2	90	3	C_6H_6	6.0	0.6		1.6	97.8		
18	RCl_2	L	H_2	90	3	THF	2.1				100		
19	$R(SCN)_2$	L	H_2	90	3	C_6H_6	1.5			1.0	99.0		
20	$RBr_2 + SnCl_2$	L	H_2	90	3	C_6H_6 + MeOH[l]	10.2	1.8		0.9	97.3		
21	$RBr_2 + SnCl_2$	L	H_2	90	12	C_6H_6 + MeOH[l]	5.0				100		
22	$RBr_2 + SnCl_2$	Ol	H_2	90	12	C_6H_6 + MeOH[l]	0			100			
23	RCl_2	L	H_2	90	3	C_6H_6 + MeOH[l]	1.7				100		
24	$RCl_2 + SnCl_2$	L	H_2	90	3	C_6H_6 + MeOH[l]	3.2	0.6		0.3	99.1		

[a] R = $[(C_6H_5)_3P]_2Ni$. [b] L = methyl linoleate, Ol = methyl oleate. [c] H_2 = 39.1 atm of hydrogen, N_2 = 27.2 atm of nitrogen. [d] C_6H_6 = benzene, THF = tetrahydrofuran (50 ml), Tol = toluene (50 ml). [e] *trans* % = per cent of *trans* isomers as elaidate. [f] U = unknown compounds. [g] S = methyl stearate. [h] M = monoene or methyl oleate. [i] D = diene or methyl linoleate. [j] c–t = *cis–trans* conjugated diene. [k] t–t = *trans–trans* conjugated diene. [l] C_6H_6 + MeOH = benzene (30 ml) and methanol (20 ml).

amounts of monoene and *total trans* isomers calculated as elaidate due to catalysis by iodo-, bromo-, and chloronickel compounds, respectively, were found to be 83.5% (84.7% *trans* isomers), 53.0% (40.9% *trans*), and 1.6% (6.0% *trans*) in a reaction medium of benzene, as shown in expt 1, 10, and 17 (Table I). Similarly, the reactions in tetrahydrofuran (THF) yielded, respectively, 83.2% monoene, 38.7% monoene, and no monoene (expt 2, 11, and 18).

2. Catalysis with Diiodobis(triphenylphosphine)nickel(II). Under 39.1 atm of hydrogen at 90° for 3 hr, methyl oleate was partially converted to the *trans* isomer (expt 6 and 7). However, under 27.2 atm of nitrogen in place of hydrogen, neither isomerization nor hydrogenation of methyl oleate was observed in either solvent (expt 8 and 9). It is particularly interesting that under nitrogen, methyl linoleate in benzene solution was hydrogenated to monoene, though in poor yield, and was converted to the *trans* isomer (expt 4). In a similar manner, methyl linoleate was converted in THF to monoene and to a mixture of *trans* isomers (expt 5). These results indicate that hydrogenation and isomerization in an inert atmosphere (nitrogen pressure) proceed more rapidly in THF than in benzene. On the other hand, under similar conditions but using 39.1 atm of hydrogen, methyl linoleate was converted to monoene in benzene solution (expt 1) as well as in THF (expt 2). Catalysis was more effective at 140° than at 90° (expt 3).

3. Catalysis with Dibromobis(triphenylphosphine)nickel(II). Methyl oleate did not react at all in the absence of hydrogen at 90° for 12 hr (expt 16) but was converted to a mixture of the *trans* isomers under hydrogen pressure (expt 15). On the other hand, under nitrogen, methyl linoleate was hydrogenated to yield 22.4% of monoene and 23.9% of the *trans* isomers (expt 14), and under hydrogen pressure, to monoene (80.5%) and *trans* isomers (57.0%) (expt 13). In addition, a small amount of stearate was observed to form concurrently (expt 10–13). These results show that in benzene solution, hydrogenation proceeds more readily under hydrogen than in its absence (expt 13 and 14). The reactions of linoleate under nitrogen form monoene and *trans* isomers in equal amounts, but, under hydrogen pressure, they yield less of the *trans* isomers than of monoene. Under 39.1 atm of hydrogen at 90° for 3 hr, methyl linoleate is converted in benzene to 53.0% monoene and 1.8% *cis–trans* conjugated diene (expt 10), but in THF to 38.7% monoene, 3.3% *cis–trans*, and 4.9% *trans–trans* conjugated dienes (expt 11), indicating that under hydrogen pressure hydrogenation proceeds more readily in benzene than in THF. Furthermore, the reaction at 140° is more favorable for hydrogenation than that at 90° (expt 12).

4. Catalysis with Other Complexes. Dithiocyanatobis(triphenylphosphine)nickel(II) has a planar configuration and thus differs from the halo complexes which are tetrahedral. The dithiocyanato complexes was found to be less effective than the halides for the hydrogenation of methyl linoleate. However, this may be due to the fact that this catalyst is less soluble in benzene than are the halo complexes.

Mixtures of the halo complexes and tin(II) chloride are less effective catalysts in a mixture of benzene and methanol than the pure halo complexes in benzene since the halo complexes are unstable in methanol solution.

Discussion

Bis(triphenylphosphine)nickel halides are effective homogeneous catalysts for both selective hydrogenation and isomerization of unsaturated compounds, thus resembling the mixture of dichlorobis(triphenylphosphine)platinum(II) and tin(II) chloride described earlier.[2a] It is especially interesting that with nickel complexes hydrogenation takes place more rapidly than isomerization. For example, the diiodo complex converted linoleate to monoene more rapidly than it changed oleate to the *trans* isomers in benzene solution under hydrogen pressure (expt 1 and 6). Similarly, in THF, linoleate was converted almost entirely to monoene, but oleate was only partially isomerized to the *trans* isomers (expt 2 and 7). Similar results were obtained with the bromo complex (expt 13 and 15). In the absence of hydrogen, neither the dibromo nor the diiodo catalyst brought about isomerization of oleate, but hydrogenation of linoleate occurred.

Two points are worthy of special note.

(1) Linoleate undergoes both rearrangement and reduction in an inert atmosphere (nitrogen), just as it does under hydrogen, though to a lesser extent. This might have been expected in those experiments in which THF was used as the solvent, for THF loses hydrogen fairly readily. It is unexpected, however, in the experiments in which benzene was used as the solvent. It may be that, in these cases, the methyl linoleate disproportionates to give monoenate and polyunsaturated esters. This point remains to be tested.

(2). Oleate undergoes *cis–trans* isomerization under hydrogen pressure, but not under nitrogen pressure.

We are of the opinion that, in an atmosphere of hydrogen, the catalyst combines with elemental hydrogen to form a hydrido complex which reacts with a double bond to bring about *cis–trans* rearrangement and migration. After the double bonds have become conjugated, reduction takes place as shown in our previous reports.[2]

No reaction intermediates were isolated in our experiments. However, several interesting papers have been published recently, suggesting that isomerization reactions of olefins take place through pathways involving π-allylmetal hydride intermediates[12] and the activation of hydrogen by metal complexes proceeds *via* an intermediate involving the expansion of the coordination sphere of the metal ion.[2,13]

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Organometallic Exchange Reactions. VI. Lithium-7 and Proton Nuclear Magnetic Resonance Spectra of the Phenyllithium–Diphenylmagnesium and Phenyllithium–Diphenylzinc Systems in Ether[1]

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Abstract: Proton and ^{7}Li spectra of ether solutions of phenyllithium with diphenylmagnesium and diphenylzinc have been examined over a large temperature range. Lithium-7 spectra show that the complex $Li_2M(C_6H_5)_4$ (M = Mg or Zn) is formed in solution when the Li:M ratio is ≥ 2, but no 3:1 complex is present, in contrast to the methyl systems. Furthermore, a 1:1 complex, $LiM(C_6H_5)_3$, appears to occur when Li:M < 2. Lithium and phenyl group exchange between phenyllithium and $Li_2M(C_6H_5)_4$ has been examined in the temperature range +34 to −58°. The lithium exchange parameters are very similar for Zn and Mg; the process is possibly rate-determined by formation of solvent-separated ion pairs. Phenyl group exchange is slower than lithium exchange; it appears to involve dissociation of the complex as a rate-determining step.

Wittig and co-workers have studied the reactions of phenyllithium with diphenylmagnesium or diphenylzinc[3] and have isolated complexes of 1:1 stoichiometry, $LiMg(C_6H_5)_3$ and $LiZn(C_6H_5)_3$. With zinc, they isolated an additional complex, $Li_3Zn_2(C_6H_5)_7$. They conclude further that the 1:1 complexes are dissociated in ether at room temperature and that the magnesium complex is dissociated to the greater extent.

On the other hand, studies of the corresponding methyl systems, methyllithium + dimethylmagnesium or dimethylzinc, indicate that the stoichiometry of the complexes is 2:1. Hurd succeeded in isolating a 2:1 complex, $Li_2Zn(CH_3)_4$, by adding methyllithium to di-

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[1] The research was supported by the National Science Foundation.

[2] Alfred P. Sloan Research Fellow.

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