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# Homogeneous Hydrogenation of Methyl Linoleate by Means of Nickel and Rhodium Complexes in Dimethylformamide

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With sodium borohydride in dimethylformamide solution, tris(pyridine)trichlororhodium and nickel chloride give complexes which are stable to hydrogen, and act as effective catalysts for homogeneous hydrogenation. Methyl linoleate is hydrogenated to give mainly the *cis*- and *trans*-monoenoic product by the nickel and rhodium complexes, respectively, and at the rhodium complex with considerable translocation of the olefinic bond. Improved methods of analysis by NMR and mass spectrometry are described.

## INTRODUCTION

We have shown that tris(pyridine)trichlororhodium in solution in dimethylformamide is stable to reduction to the metal by means of sodium borohydride, and that the combination $py_3RhCl_3$/DMF/$NaBH_4$ constitutes a highly active system for homogeneous hydrogenation by molecular hydrogen (*1*). An active complex $py_2(DMF)RhCl_2(BH_4)$ has been characterized (*1*), and the catalyst system has been shown to be effective for the hydrogenation of olefins (*1*), acetylenes (*2*), 3-keto-$\Delta^4$-steroids (*3*), and for the groupings —N:CH—, —N:N—, and —$NO_2$ (*4*).

This active rhodium catalyst was recognized from a survey of the behavior of a range of transition metal salts towards sodium borohydride in dimethylformamide solution (*5*). Of the other metal salts examined, nickel chloride was found to exhibit a similar albeit smaller catalytic activity under these conditions.

We now report a brief comparative study of the use of the rhodium and nickel salt activated with sodium borohydride for the hydrogenation of methyl linoleate in dimethylformamide solution. This was undertaken in the light of an earlier examination (*6*) of the selectivity of a group of complexes, $(Ph_3P)_2MX_2$, towards hydrogenation and isomerization of 1-octene. It was found that the rate of hydrogenation of 1-octene vs isomerization to 2-octene increases in the sequence: Pd < Pt < Ni, where X = Cl, Br, I. Since conjugative isomerization is a considerable factor in determining selectivity in the hydrogenation of the 1,4-diene grouping of linoleate, we anticipated that the $NiCl_2$/DMF/$NaBH_4$ catalyst might show some advantage in this respect.

## EXPERIMENTAL

**Methyl linoleate** (99% from Sigma Chemical Co.) was distilled (bp 150–155°C/1.2 mm Hg) rapidly in small scale apparatus *in vacuo* and stored under nitrogen at 0°C.

**Hydrogenations** were carried out in carefully degassed dimethylformamide which was then saturated with hydrogen. Hydrogenations were followed by the hydrogen uptake at constant pressure in a differential form of apparatus and by sampling *via* a serum cap.

**The catalysts** were prepared in dimethylformamide and equilibrated by shaking under hydrogen:

(a) Tris (pyridine)trichlororhodium (*7*) (9 mg) in degassed dimethylformamide (10



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ml) was treated with powdered sodium borohydride (0.8 mg) and the brown solution shaken under hydrogen.
(b) Hydrated nickel chloride ($NiCl_2 \cdot 6H_2O$, 14 mg) in degassed dimethylformamide (10 ml) was treated with sodium borohydride (2 mg) and shaken under hydrogen.

To the solutions prepared in (a) and (b), methyl linoleate (100 mg) was injected *via* a serum cap.

When hydrogenation was complete the product was taken into hexane by repeated extraction and dimethylformamide removed from the extract by washing with water.

**The analyses** were carried out using a 9 ft column of polyethylene glycol succinate at 175–180°C.

**Methoxymercuration.** Methyl oleate, elaidate, the hydrogenation product or other olefin were treated with mercuric acetate (1.2 molar equivalents) in dry methanol and stirred magnetically in the dark for 24 hr.

(i) To obtain the methoxy derivative for mass spectral analysis the reaction mixture was treated with an excess of sodium borohydride and after a few minutes any excess borohydride was destroyed by adding a little acetic acid. The solution was then evaporated *in vacuo* and the residue extracted with ether. After thorough washing with water the ether solution was evaporated *in vacuo*. The monomethoxy derivatives, isolated by thin layer chromatography on silica gel in benzene/ether (4:1), $R_f$ 0.6, were extracted from the silica gel by means of chloroform.

Using this procedure with an excess of mercuric acetate, methyl linolenate gave mono-, di-, and tri-methoxy derivatives of $R_f$ 0.5, 0.35 and 0.2, respectively, and methyl linoleate gave mono- and di-methoxy derivatives of $R_f$ 0.6 and 0.35.

(ii) To obtain the methoxymercuric acetate adducts for NMR examination the reaction mixture in methanol was carefully evaporated *in vacuo* without heating (temperature <30°C). The residue was extracted into chloroform and the extract washed well with water. Removal of solvent and chromatography on silica gel in benzene/ether (4:1) removed any organic material, the methoxymercuric adducts remaining on the base line. Further development in *n*-propanol/acetic acid (100:1) gave the adducts as a spot of $R_f \sim 0.5$ which could be extracted into a solvent for NMR analysis. Table 1 summarizes the results for various pairs of olefins RCH=CHR′.

TABLE 1
NMR Analysis of Pairs of Olefins RCH=CHR′ (See Text)

| R | R′ | *cis*[a] | *trans*[a] |
|---|---|---|---|
| $CH_3(C_2H)_7$ | $(CH_2)_7CO_2Me$ | 6.84 | 6.93 |
| $CH_3CH_2$ | $CH_2CH_3$ | 6.80 | 6.85 |
| $CH_3$ | *n*-$C_5H_{11}$ | 6.72 | 6.80 |
| *n*-$C_3H_7$ | *n*-$C_3H_7$ | 6.80 | 6.85 |
| $CH_3$ | *i*-$C_3H_7$ | 6.82 | 6.86 |

[a] NMR signal for CH—OC$H_3$ protons in the methoxymercuric acetate adduct in benzene solution.

## Results and Discussion

The $py_3RhCl_3/NaBH_4$ combination was found to effect very rapid catalysis of the hydrogenation of methyl linoleate in dimethylformamide solution (5 ml $H_2$/min uptake with $py_3RhCl_3$ $2 \times 10^{-3}$ *M* and $NaBH_4$ $2 \times 10^{-3}$ *M* with methyl linoleate $2 \times 10^{-2}$ *M* in dmf). After the uptake of 1 molar equivalent of hydrogen, the product, extracted by means of hexane, showed a composition: linoleate, 2%; stearate, 3%, and monoenoate 95%, by GLC analysis. However, the relative intensity of the infrared absorption at 965 $cm^{-1}$ in comparison with methyl elaidate showed that the monoenoic ester was mainly of the *trans* configuration. Formation of the *trans* olefin is no doubt the basis of the marked selectivity of this catalyst, i.e., the *cis, cis*-grouping of linoleate reacts in preference to the *trans*-grouping of the monoenone product. We also infer that this rhodium catalyst is highly active for the isomerization: 1,4-diene → *trans, cis*-1,3-diene $\xrightarrow{H_2}$ *trans*-monoene.

Nickel chloride ($NiCl_2 \cdot 6H_2O$, $2 \times 10^{-2}$ *M*) with sodium borohydride ($2 \times 10^{-2}$ *M*) in dimethylformamide was found to hy-

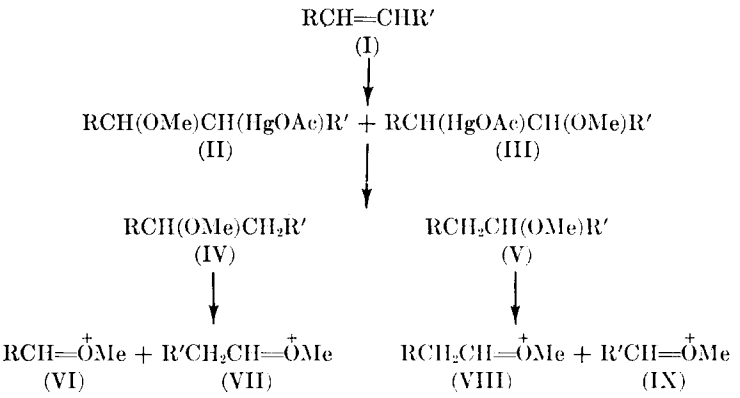
drogenate methyl linoleate ($10^{-1}$ *M*) at approximately one-tenth the rate observed with the rhodium catalyst. After uptake of 1.25 molar equivalents of hydrogen the product contained only a trace of linoleate, some 15% stearate, and 85% of monoenoic ester. Negligible ultraviolet absorption at 225 nm indicated the absence of conjugated diene, and weak infrared absorption at 965 $cm^{-1}$ showed the content of *trans* monoenoic ester to be low.

This result confirmed the expectation that isomerization would be minimized with the nickel catalyst system. It also established that hydrogenation may be effected by means of one of the less costly transition metal salts in an appropriate solvent such as dimethylformamide,[1] and also without the use of complex $\pi$-acceptor stabilizing ligands.

convenient means both of locating an olefinic bond, *via* mass spectrometry, and also of making an independent estimate of the *cis/trans* content of a mixture by means of the NMR spectrum of the methoxymercuric acetate adduct.

Methoxymercuration of an unsymmetrical monoolefin (I) followed by reduction with sodium borohydride leads to isomeric methoxy derivatives (IV) and (V) which in the mass spectrometer will give principal fragment ions (VI), (VII), (VIII) and (IX).

The methoxy derivatives from methyl oleate and methyl elaidate (I,R = $CH_3(CH_2)_7$, and R′ = $(CH_2)_7CO_2Me$) gave in the mass spectrometer, intense ions of m/e 157, 171, 201 and 215, corresponding to (VI), (VIII), (IX) and (VII) respectively (*9*).




The well-known method (*8*) of analysis based on the ratio of absorption intensity in the infrared spectrum at 965 $cm^{-1}$ to that at 1730 $cm^{-1}$ indicates the stereochemistry, but not the location of the olefinic center. Moreover, the estimation of a minor amount of trans olefinic component from a rather small intensity of absorption at 970 $cm^{-1}$ is difficult. We have therefore developed a procedure based on methoxymercuration as a

The product of hydrogenation of methyl linoleate obtained by means of $NiCl_2$/$NaBH_4$/DMF gave by this methoxymercuration/demercuration procedure a methoxy derivative showing a similar group of ions, viz. m/e 201 and 215 ($MeO^+$=$CH(CH_2)_nCO_2Me$, $n = 7$ or 8), and m/e 157 and 171 ($CH_3(CH_2)_nCH{=}O^+Me$, $n = 7$ or 8). Minor peaks at m/e 243, 229, and 187, corresponding to ions $MeO^+{=}CH(CH_2)_nCO_2Me$, $n = 10$, 9, 6, were also observed.

These results indicate that with this Ni-catalyst the olefinic center in methyl linoleate which is more remote from the —$CO_2Me$ group is preferentially hydrogenated, i.e., route (i) is faster than (ii):

[1] A referee has drawn our attention to an earlier paper by P. N. Rylander, N. Himelstein, D. R. Steele and J. Kreidl; *Englehard Ind. Tech. Bull.* **3**, 61 (1962) indicating the advantage of dimethylformamide.

$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2Me$$

(i) ↙ ↘ (ii)

$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$ $CH_3(CH_2)_4CH{=}CH(CH_2)_{10}CO_2Me$

By contrast the mainly *trans*-monoenoic ester obtained from methyl linoleate by means of the $py_3RhCl_3/NaBH_4$ catalyst gave a methoxy derivative showing in the mass spectrometer ions corresponding to a large number of positional isomers, i.e., formation of the *trans* olefin is associated with extensive olefin isomerization.

As indicated above, methoxymercuration also offers a convenient means of estimating the proportions of *cis*- and *trans*-monoenoic ester in the methyl linoleate hydrogenation product. The methoxymercuric acetate adducts of methyl oleate and elaidate which may be isolated by tlc, were found to show in the NMR spectrum in benzene signals for the methyl ether protons at 6.84 and 6.93 $\tau$, respectively. The mono- and bis-methoxymercuric acetate adducts of methyl linoleate show corresponding signals at 6.70 and 6.80 $\tau$. A mixture of all three esters gave a derivative showing the spectrum of Fig. 1. Applied to the product of $NiCl_2/NaBH_4$ catalyzed hydrogenation of methyl linoleate the relative areas of the 6.84 and 6.93 $\tau$ signals indicated a ratio of *cis*- to *trans*-monoenoic ester of 7.5:1, and

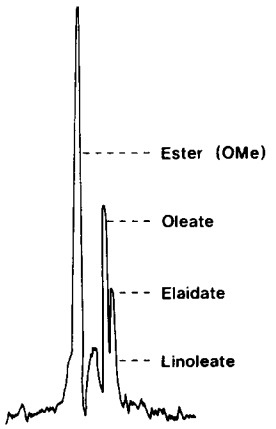



FIG. 1. NMR spectrum of methoxymercury acetate derivatives of methyl oleate, elaidate and linoleate in benzene.

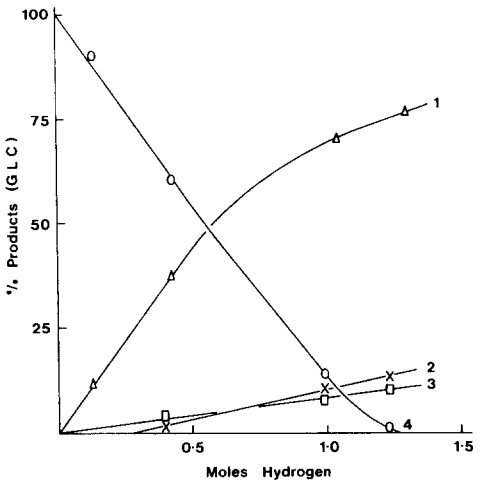



FIG. 2. Product distribution during the hydrogenation of methyl linoleate using the $NiCl_2/NaBH_4$ system in dimethylformamide: (1) *cis*-mono-enoate, (2) stearate, (3) *trans*-mono-enoate, (4) linoleate.

analysis of samples withdrawn during hydrogenation gave the data of Fig. 2. Similarly the NMR spectrum of the methoxymercuric acetate adduct of the product of hydrogenation by means of the $py_3RhCl_3/NaBH_4$ catalyst showed only the 6.93 $\tau$ signal for —CH—OC$H_3$ protons. Thus NMR analysis of the methoxymercuric acetate adducts confirms and supplements the long established infrared method of analysis. The principle of the method derives from the —OMe and —HgOAc groups being *anti*- and *gauche*-related in the methoxymercuric acetate adducts of a *trans*- and a *cis*-olefin, respectively, in the optimal conformation where the alkane residues are in *anti* relationship. Precedents are provided in the work of Waters (*10*), and we have added further instances for various pairs of *cis*- and *trans*-olefins (*cf.* experimental). The application of the procedure to lipids was described (*11*) after our work was completed.

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