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Reduction of Organic Compounds with $NaBH_4$-Transition Metal Salt Systems. IV.[1] Selective Hydrogenation of Olefines in Unsaturated Esters

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Hydrogenation of unsaturated esters was performed with $NaBH_4$-transition metal salt systems.

Nickel, cobaltous and cupric salts were effective metal salts for reduction of olefinic esters. Hydrogenation of the olefinic bonds proceeded quantitatively to afford the corresponding saturated esters when using one of the following pairs: $NiCl_2 \cdot 6H_2O$ (0.1 mole)-$NaBH_4$ (2 moles), $CoCl_2 \cdot 6H_2O$ (0.25 moles)-$NaBH_4$ (10 moles) and $CuCl_2 . 2H_2O$ (0.3 moles)-$NaBH_4$ (6 moles) per mole of I.

In previous papers we reported the reduction of nitrile[1,3] and nitro[3-5] compounds with $NaBH_4$-trasition metal salt system.

This paper concerns the selective hydrogenation of C-C double bonds in unsaturated esters.

There are many cases in organic synthesis that need saturated esters derived from corresponding unsaturated compounds by selective reduction of olefinic bonds.

Selective reduction of these olefines has usually been carried out by catalytic hydrogenation[6] or electrochemical reduction.[7] $NaBH_4$ has been known to be lacking in the ability to reduce these compounds. Strongly polarized olefines, however, like nitroolefines[8] or dimethyl Isopropylidenemalonate,[9] are well known to be reduced to the corresponding saturated nitro compounds or esters at room temperature. Ethyl cinnamate afforded ethyl hydrocinnamate in only a 25% yield under the same condition.[9]

Brown, *et al.*[10] obtained cinnamyl alcohol, 3-phenylpropanol and methyl hydrocinnamate in 17, 15 and 13% yields respectively by reduction of methyl cinnamate with ten-fold moles of $NaBH_4$ in boiling methanol.

The $NaBH_4$-transition metal salt systems, which had the advantage that reduction of organic compounds could be carried out in hydroxylic solvents just like $NaBH_4$ reduction, were adapted to the reduction of olefines which could hardly be reduced by $NaBH_4$ alone.

Result

Reduction of Methyl Cinnamate I with $NaBH_4$-Transition Metal Salt Systems

When $NaBH_4$ (10-fold moles per I) was added to the MeOH containing I and various metal salts (2-fold moles per I) at room temperature, black or white ($ZnCl_2$ or $SnCl_4 \cdot 5H_2O$) precipitates appeared along with generation of a gas.

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By gas chromatographic analysis of the filtrate of the reaction mixture, only methyl hydrocinnamate II, which was the selective reduction product of I in its olefinic bond, was detected and neither the starting material I nor any other product was observed when $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$ were used as metal salt. $AlCl_3$ and $FeCl_3$ were thought to be inert though a small amount of methyl hydrocinnamate was formed in the reduction system, because the amount of II was almost the same as with $NaBH_4$ reduction. $CrCl_3 \cdot 6H_2O$, $SnCl_4 \cdot 5H_2O$, $ZnCl_2$ or $CdCl_2 \cdot 5/2H_2O$, however, proved to promote degradation of $NaBH_4$ and not to reduce I.

Table I shows the results of quantitative estimation of II formed when using various metal salts.

TABLE I. Reduction of Methyl Cinnamate (I) with $NaBH_4$-Transition Metal Salt (MX) Systems

MX	Methyl hydrocinnamate (%)	MX	Methyl hydrocinnamate (%)
$NiCl_2 \cdot 6H_2O$	quantitative	$FeCl_3$	10
$CoCl_2 \cdot 6H_2O$	quantitative	$ZnCl_2$	0
$CuCl_2 \cdot 2H_2O$	quantitative	$CrCl_3 \cdot 6H_2O$	0
$PdCl_2$	quantitative	$(SnCl_4 \cdot 5H_2O)$[b]	0
$(AlCl_3)$[b]	10	None	10

a) reaction condition: I (5 mmole), $NaBH_4$ (50 mmole), MX (10 mmole) in MeOH (100 ml) at 20°
b) These metal salts do not belong to transition metal salts.

Brown, *et al.*[11] reported that the black precipitate obtained from the reaction of $NaBH_4$ and Ni $(OAc)_2$ in EtOH was stronger as the catalyst of catalytic hydrogenation of carbon-carbon double bonds than Raney Nickel. Takegami, *et al.*[12] described in their report that the black precipitate formed in the $NaBH_4$–$NiCl_2 . 6H_2O$-MeOH system was more effective as hydrogenation catalyst of styrene than the Nickel boride catalyst made in H_2O and moreover, catalytic activity varied according to the molar ratios of $NaBH_4$ and Nickel salt used.

TABLE II. Influence of the amount of Metal Salts in Reduction of Methyl Cinnamate (I) with $NaBH_4$-MX Systems

MX (moles per mole of (I)	Methyl hydrocinnamate (%)	MX (moles per mole of (I))	Methyl hydrocinnamate (%)
0.01 (Ni)[a]	30	0.2 (Co)	96
0.01 (Co)[b]	40	0.25 (Ni)	*ca.* 100
0.01 (Cu)[c]	12	0.25 (CO)	*ca.* 100
0.03 (Ni)	84	0.3 (Cu)	*ca.* 100
0.05 (Co)	80	2.0 (Ni)	*ca.* 100
0.05 (Cu)	23	2.0 (Co)	*ca.* 100
0.1 (Ni)	*ca.* 100	2.0 (Cu)	*ca.* 100
0.1 (Co)	84		
0.15 (Cu)	88		

a) Ni: $NiCl_2 \cdot 6H_2O$
b) Co: $CoCl_2 \cdot 6H_2O$
c) Cu: $CuCl_2 \cdot 2H_2O$
reduction condition
(I) : 5 mmole
$NaBH_4$: 50 mmole, solvent: MeOH (100 ml), temperature: 20°

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In our $NaBH_4$-transition metal salt systems, hydrogenation of olefinic bonds may proceed catalytically, and then the effect of the molar ratios of $NaBH_4$ and metal salts upon the formation of II was examined by using $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$, which were effective in the preliminary experiments described above, at various salt concentration.

Table II shows the results obtained.

In the reduction system, the hydrogenation of I proceeded quantitatively when the molar ratios of $NaBH_4$-$NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ were above 100, 40 and 33 respectively. To examine the minimal need of $NaBH_4$, reduction of I was performed by various amounts of $NaBH_4$ with 2-, 3- and 4- fold moles of $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$.

Fig. 1 shows the results.

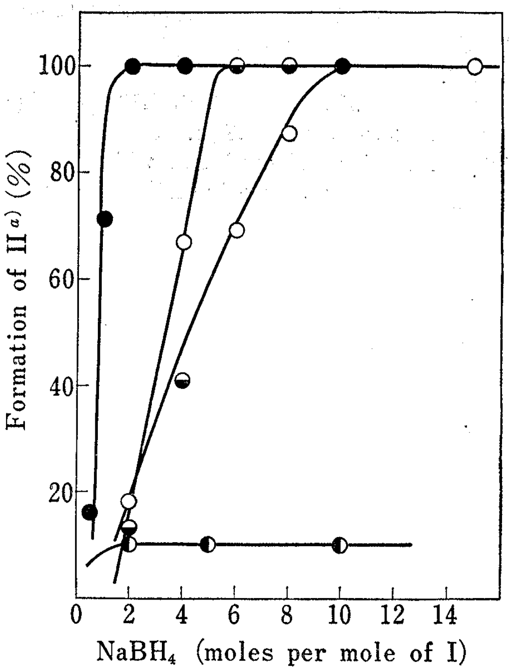

Fig. 1. Effect of the Amount of $NaBH_4$ on Reduction of Methyl Cinnamate (1)[b] in MeOH at 20°

—●—: $NaBH_4$–$NiCl_2 \cdot 6H_2O$ (0.5 mmole)
—○—: $NaBH_4$–$CoCl_2 \cdot 6H_2O$ (1.25 mmole)
—◒—: $NaBH_4$–$CuCl_2 \cdot 2H_2O$ (1.5 mmole)
—◐—: $NaBH_4$ alone
a) methyl hydrocinnamate
b) Five mmole of I was used.

The minimal amounts of $NaBH_4$ for the quantitative reduction of I to II proved to be 10, 50 and 30 mmoles in the case of using $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ respectively.

It was, therefore, supposed to be most suitable for the reduction of olefines to employ 2-fold moles of $NaBH_4$ and 0.1-fold moles of $NiCl_2 \cdot 6H_2O$ per mole of I.

To confirm the reduction product of I, 8.1 g of I was reduced under the most suitable conditions and 6.0 g of colorless liquid (bp 115—115.5°) (15 mmHg) was obtained (74% yield as II).

The liquid was identical with the authentic methyl hydrocinnamate in IR spectrum and gas chromatography.

It is generaly said that the susceptibility of C-C double bond to reduction depends upon its polarity, and especially, lone double bonds in a molecule resist hydrogenation.

The adaptability of the reduction systems was investigated by reduction of hydroxyethyl methacrylate (III) and methyl oleate (IV) with the most suitable amount of $NaBH_4$-$NiCl_2 \cdot 6H_2O$ described above, and it was found that III was quantitatively reduced to hydroxyethyl isobutylate gas chromatographically and methyl stearate (mp 36.0—36.7°) was obtained in a 92% yield by the reduction of IV.

From the above experimental results, the reduction system was presumed to be capable of use as the general reduction method for olefines.

Experimental

All melting points were determined on a micro hot-stage and were uncorrected.

The IR spectra were measured with a Hitachi Model EPI G3 spectrophotometer.

Gas chromatographic analysis was performed with a Shimazu gas chromatograph Model GC-2C equipped with a hydrogen flame detector on the following column.

Column——polyethylene glycol 6000 on Celite 545, 1.5m.

Reduction of Methyl Cinnamate (1)[13] with $NaBH_4$-$NiCl_2 \cdot 6H_2O$ System——I (8.1 g, 50 mmoles) and $NiCl_2 \cdot$

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[13] IR cm^{-1}: 1715 (C=O), 1640 (C=C). t_R=20 min (150°).

$6H_2O$ (1.19 g, 5 mmoles) were dissolved in MeOH (200 ml). Adding $NaBH_4$ (3.78 g, 100mmoles) in small portions to the solution caused evolution of hydrogen gas and it turned black. The reaction temperature was kept at 20° by ice cooling. After addition of $NaBH_4$ was complete, it was stirred for one hour at room temperature. The black precipitate formed was filtrered and washed with MeOH.

The filtrate and washings were combined and condensed *in vacuo* to about 50 ml. To the residual solution, 100 ml of H_2O was added and the solution was extracted with ether (50 ml × 5). After washing with H_2O and drying, ether was removed. The colorless transparent liquid (6.8 g) thus obtained was distilled *in vacuo* to give 6.0 g of II, bp 115—115.5 (15 mmHg), 74% yield.
IR cm^{-1}: 1740 (C=O). t_R: 8min (150°).

Reduction of Hydroxyethyl Methacrylate (III)——III(1.18 g, 10 mmoles) and $NiCl_2 \cdot 6H_2O$ (0.38 g, 2 mmoles) were dissolved in MeOH (100 ml) and treated with $NaBH_4$ (1.13 g, 30 mmoles) at 20°. After filtration of the reacton mixture, a portion (4 μl) of the filtrate was analysed with a gas chromatograph (150°). Only the peak of hydroxyethyl isobutylate ($t_R = 8$ min) was observed and none of III ($t_R = 13$ min) was detected.

Reduction of Methyl Oleate (IV)——IV (14.8 g) was reduced in the same way as described above to give a transparent oil (13.7 g). It was crystallized with ice cooling, mp 35—36°. Recrystallization from MeOH afforded colorless plates, which was confirmed by undepression of the mixed melting points and IR spectra with an authentic methyl stearate.