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Catalytic Hydrodehalogenation of Some Organic Halides by Hydrogen Transfer from Lithium Formate in the Presence of Ruthenium and Rhodium Complexes

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Organic halides react with lithium formate in the presence of ruthenium and rhodium phosphine complexes as homogeneous catalysts in refluxing dioxane producing the corresponding dehalogenated compounds in moderate yields.

INTRODUCTION

The catalytic transfer hydrogenation and hydrogenolysis of unsaturated organic functional groups by appropriate hydrogen donors other than molecular hydrogen is still an area of considerable interest and has recently been reviewed.¹ Combination of a selective, mild and effective catalyst with hydrogen donor results in replacement of the heteroatom or group by hydrogen. Among various hydrogen donors, formic acid and its salts continue to be explored in catalytic transfer hydrogenation of some functional groups under moderate reaction conditions.²⁻⁷ Availability and ease of handling of these hydrogen donors offer some advantages over the other sources of hydrogen already used in hydrogen transfer reactions. The catalytic hydrodehalogenation of organic halides is a well known reaction of both preparative and environmental significance.⁸ Therefore, several reports have appeared on this subject using various hydrogen donors, along with heterogeneous or homogeneous catalysts.⁹⁻²⁰ Thus, the salts of formic acid were reported to be efficient hydrogen donors in combination with palladium on carbon catalyst.^{3-9,15} Homogeneous transition metal catalysts have been less explored, being limited to palladium phosphine complexes.^{10,11} The present study deals with the hydrodehalogenation of some organic halides with lithium formate as hydrogen donor in the presence of some transition metal complexes other than palladium complexes.

EXPERIMENTAL

Materials

Lithium formate was prepared by stepwise addition of a stoichiometric quantity of lithium carbonate to formic acid. The solution was evaporated to dryness. Commercial organic halides and dioxane were purified by standard methods.

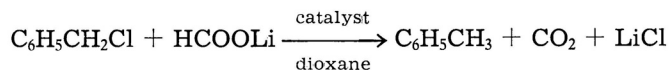
Transition metal complexes $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}^{21}$, $\text{RhH}(\text{PPh}_3)_4^{22}$, $\text{RhHCO}(\text{PPh}_3)_3^{23}$, $[\text{Rh}(\text{COD})\text{Cl}]_2^{24}$, $\text{CoCl}_2(\text{PPh}_3)_2^{25}$, and $\text{NiCl}_2(\text{PPh}_3)_2^{26}$ were prepared by methods reported in literature, while $\text{RuCl}_2(\text{PPh}_3)_2$, $\text{RuHClCO}(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{PPh}_3)_4$ were available from a previous study of catalytic hydrogen transfer reactions.²⁷

Reaction Procedure

In a typical procedure, a two-necked 50 ml round-bottomed flask was charged with dioxane (10 ml) and lithium formate (6 mmol). The flask was equipped with a reflux condenser, nitrogen inlet and outlet. After replacing the air by nitrogen, the catalyst (0.05 mmol) was added and the system was heated to constant boiling. The reaction was initiated by addition of organic halide (2 mmol) flushed with nitrogen before addition. The reaction samples were withdrawn with an injection syringe at appropriate time intervals. Reaction products were analyzed by GLC using HP 5790 apparatus equipped with a 1.8 m long column packed with either 10% Apiezon L or 10% OV 17 supported on Chromosorb WHP 100/120. Identification of the products was made by comparing the retention times of authentic samples.

RESULTS AND DISCUSSION

For the initial study, benzyl chloride was chosen, which might be hydrodehalogenated to toluene according to the scheme:



Blank experiments were carried out in the absence of lithium formate but in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.05 mmol) in boiling dioxane. Hydrodehalogenation of benzyl chloride does not take place under these conditions. Results of transfer hydrodehalogenation using lithium formate as hydrogen donor catalyzed by ruthenium and rhodium complexes in refluxing dioxane are presented on Table I. Their catalytic activity is comparable to that of palladium complexes which were already reported as excellent catalysts for hydrodehalogenation of organic halides.^{10,11} In additional experiments, the

TABLE I

Catalytic transfer hydrodehalogenation of benzyl chloride using lithium formate as hydrogen donor in the presence of ruthenium and rhodium phosphine complexes as catalysts^a

Catalyst	Yield of toluene ^b %
$\text{RuCl}_2(\text{PPh}_3)_3$	66
$\text{RuHClCO}(\text{PPh}_3)_3$	60
$\text{RuH}_2(\text{PPh}_3)_4$	62
$\text{RuCl}_2(\text{PPh}_3)_3/3 \text{ PPh}_3$	48
$\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}/6 \text{ PPh}_3$	33
$\text{RhH}(\text{PPh}_3)_4$	42
$\text{RhHCO}(\text{PPh}_3)_3$	26
$[\text{Rh}(\text{COD})\text{Cl}]_2/4 \text{ dppe}^c$	33

^a Reaction conditions; benzyl chloride 2 mmol, lithium formate 6 mmol, and catalyst 0.5 mmol were heated in refluxing dioxane 10 ml for 6 hrs.

^b Determined by GLC using the internal standard method

^c 1,2-Bis(diphenylphosphino)ethane

other potential homogeneous catalysts $\text{CoCl}_2(\text{PPh}_3)_2$ and $\text{NiCl}_2(\text{PPh}_3)_2$ exhibited no catalytic activity. Hydrodehalogenation of benzyl chloride in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ can also be achieved by lithium formate prepared *in situ* using equimolar quantities of formic acid and lithium carbonate. The reaction is inhibited by addition of an excess of formic acid. The reaction takes place also using formic acid alone (6 mmol), but only low yield (6%) of toluene was achieved. This result confirms the previous report that formic acid salts are more active hydrogen donors than formic acid itself.²⁸ The results of the catalytic hydrodehalogenation of some other organic halides besides benzyl chloride are presented in Table II. No dimeric or other byproducts

TABLE II
Hydrodehalogenation of some organic halides by lithium formate catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3^a$

Organic halide	Hydrodehalogenation product	Yield %
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	$\text{C}_6\text{H}_5\text{CH}_3$	66
$2\text{-ClC}_6\text{H}_4\text{CH}_2\text{Cl}$	$2\text{-ClC}_6\text{H}_4\text{CH}_3$	63
$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	$\text{C}_6\text{H}_5\text{CH}_3$	60
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br}$	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$	14
$4\text{-BrC}_6\text{H}_4\text{Br}$	$\text{C}_6\text{H}_5\text{Br}$	17

^a Carried out in refluxing dioxane for 6 hr, with 2 mmol of organic halide, 6 mmol of lithium formate and 0.05 mmol of $\text{RuCl}_2(\text{PPh}_3)_3$.

have been detected under the reaction conditions used. Conversion depends mainly on the character of the C atom bearing a halogen. Detailed kinetic analysis of this reaction in the presence of ruthenium and rhodium complexes as homogeneous catalysts is in progress.

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SAŽETAK

Katalitička hidrodehalogenacija nekih organskih halogenida prijenosom vodika s lijeva formijata u prisutnosti kompleksnih spojeva rodija i rutenja

R. Marčec

Organski halogenidi reagiraju s litijevim formijatom u prisutnosti fosfinskih kompleksnih spojeva rutenija i rodija kao homogenh katalizatora u vrijućem dioksanu i transformiraju se u odgovarajuće dehalogenirane spojeve u umjerenim iskorištenjima