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Preliminary communication

ARYLATION OF THE REFORMATSKY REAGENT CATALYZED BY ZEROVALENT COMPLEXES OF PALLADIUM AND NICKEL

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Summary

The Reformatsky reagent $BrZnCH_2COOEt$ reacts with aromatic organometallic complexes of nickel and palladium $ArMXL_2$ (M = Ni, Pd; X = Cl, Br, I; L = $(C_6H_5)_3P$) to give aryl acetic acid esters in good to moderate yields. The reaction can be catalyzed by use of zerovalent complexes of palladium and nickel which undergo oxidative addition with aromatic halides.

We have shown that organometallic compounds such as RMgX can react with organopalladium compounds such as $C_6H_5PdI[(C_6H_5)_3P]_2$ to give coupling products C_6H_5R [1]. This kind of reaction is now widely recognized as one of the key reactions in the coupling of Grignard reagents or organolithium compounds with aromatic halides catalyzed by organometallic complexes of palladium and nickel [1—4]. We now show that this coupling can be extended to the Reformatsky reagent $BrZnCH_2COOEt$.

First, we summarize in Table 1 results of a preliminary study of the reaction between $C_5H_5MX[(C_6H_5)_3P]_2$ [5,6] and $BrZnCH_2COOEt$. Hexamethylphospho-

TABLE 1

$BrZnCH_2COOEt + C_6H_5MX[(C_6H_5)_3P]_2 \rightarrow C_6H_5CH_2COOEt$

$C_6H_5MXL_2$ [a]	Yield (%) of $C_6H_5CH_2COOEt$ [b]	Yield (%) of $C_6H_5C_6H_5$ [b]
$C_6H_5PdIL_2$	43	34
$C_6H_5PdBrL_2$	53	48
$C_6H_5PdClL_2$	52	39
$C_6H_5NiIL_2$ [c]	70	29

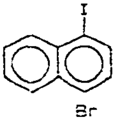
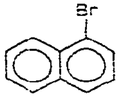
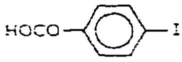
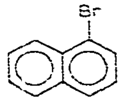
[a] L = $(C_6H_5)_3P$, solvent: methylal/HMPA (1/1 by volume), 4 hours reflux.
[b] Yields by CPV, yield of biphenyl is the percentage of the complex $C_6H_5MXL_2$ converted into biphenyl.
[c] 4 hours at 0°C.

ramide has to be added to the solvent methylal (dimethyloxymethane) in order to obtain fair yields. Biphenyl is always a by-product. Reaction seems easier when M = Ni.

In order to prepare $C_6H_5NiI[(C_6H_5)_3P]_2$ we needed $Ni[(C_6H_5)_3P]_4$ and made the latter by a novel method, in which $NiCl_2[(C_6H_5)_3P]_2$ is reduced by two equivalents of ethylmagnesium bromide in diethyl ether in the presence of two equivalents of triphenylphosphine. (This is more convenient than the published procedure involving reduction of nickel(II) complexes by diethylaluminum monoethoxide [7] or by zinc powder [8].) Owing to the instability and oxygen sensitivity of nickel(0) complexes they were used immediately for oxidative addition with aromatic halides (C_6H_5I) or for catalytic coupling (Table 2). $BrZnCH_2COOEt$ was prepared in methylal as previously described [9].

TABLE 2

$$BrZnCH_2COOEt + ArX \xrightarrow{ML_4{}^a,\ 10\%} ArCH_2COOEt$$

ArX	M	Yield (%) of $ArCH_2COOEt$	Recovered ArX (%)
C_6H_5I	Pd[b]	47	43
C_6H_5Br	Pd[c]	15	79
C_6H_5Cl	Pd	No reaction	
	Pd[d]	47	52
	Pd	No reaction	
	Pd	65[e]	traces
C_6H_5I	Ni[f]	55	39
C_6H_5Br	Ni	67	14
C_6H_5Cl	Ni	65	22
	Ni	69	traces

[a] $L = (C_6H_5)_3P$, unless otherwise specified, conditions are 3 hours reflux, solvent: methylal/HMPA (1/1 by volume), $BrZnCH_2COOEt$: 2 equivalents. Yields were not optimized.
[b] 6 hours reflux.
[c] 7 hours reflux in solvent: benzene/HMPA (1/1 by volume).
[d] No β-naphthyl acetic acid ester isomer can be detected in the product.
[e] 4 equivalents of $BrZnCH_2COOEt$ are used. Yield of isolated product. IR, NMR and mass spectra agree with the structure.
[f] Room temperature.

Secondly, we report results of a preliminary study of the catalytic coupling of $BrZnCH_2COOEt$ with some aromatic halides, catalyzed by zerovalent complexes of palladium and nickel $M[(C_6H_5)_3P]_4$ (Table 2). The solvent was always methylal/HMPA (1/1 by volume).

Nickel(0) complexes undergo oxidative addition with aromatic halides more readily than palladium(0) complexes and are more efficient in the catalysis, but care must be taken to prevent accidental oxidation of the nickel(0) complexes during the reaction (degassing of the solvents is necessary) because the Reformatsky reagent seems to be unable to reduce nickel(II) complexes. In the case of accidental oxidation the red brown solution becomes blue green and the reaction stops. Owing to the greater dilution of the $ArMXL_2$ species, only traces of biaryl are formed but the coupling necessitates longer time and the aromatic halide is not always completely consumed after 3 or 4 hours at reflux.

This reaction appears to be one of the few examples known of coupling between an enolate type reagent and an aromatic halide catalyzed by transition metal compounds, other examples include the synthesis of cephalotaxinone via an intramolecular, arylation of an enolate by an arylnickel iodide [10]; and the coupling, catalyzed by copper, of 2-bromobenzoic acid derivatives with sodiomalonic acid ethyl ester [11]. Such catalytic aromatic nucleophilic substitution is "a priori" more interesting because of its regioselectivity than arylation via a "benzyne" mechanism. Work is currently in progress to study the scope and limitations of this reaction.

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