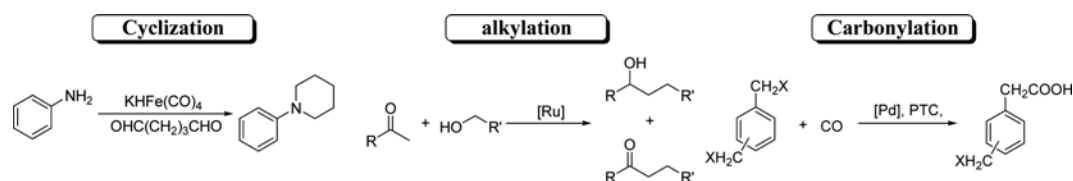


Organometallic Chemistry Meeting for 35 years: Alkylation, Carbonylation and Cyclization Reaction using Transition Metal (or inner-) Complexes as Reducing Agents or Catalysts

Sang Chul Shim[†]

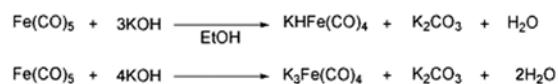
Abstract



Alkylation, carbonylation and cyclization reaction using transition metal(or inner-) complexes as reducing agents or catalysts were investigated.

Key words : Alkylation, Carbonylation, Cyclization, Reducing Agent, Catalyst

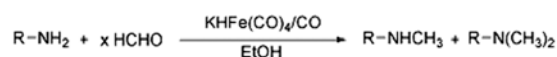
Tetracarbonylhydridoferrate prepared from pentacarbonyliron and alkali metal hydroxide has been shown to be a convenient, selective reagent for carbonylation and/or reduction of a variety of organic functional groups such as a nitro group, an acetyenic bond, olefinic bond of conjugated diene, enamine, and a,b-unsaturated carbonyl compound, alkyl halides, and olefin oxides.^[1-5]



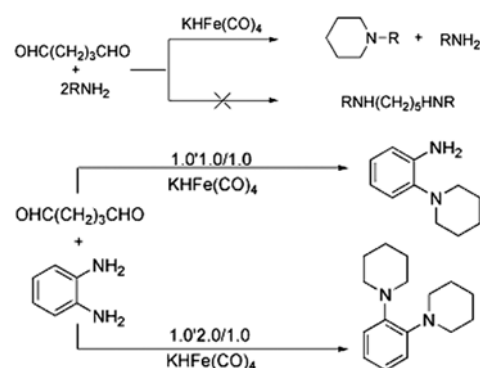
More recently, several works have demonstrated that the ferrate is effective for reductive alkylation of amine and ketones with carbonyl compounds. Several methods for the synthesis of N-alkylamine from amines and carbonyl compounds have been reported.^[6-8]

Aniline was converted into N-methyl- and N,N-dimethylaniline with tetracarbonylhydridoferrate-formaldehyde under different conditions. The formation of N-methylated anilines was highly affected by such reaction variables as reaction temperature, atmosphere,

molar ratio (the ferrate/formaldehyde/aniline), and the addition of water.



And also, when aqueous glutaraldehyde (45%) is mixed with a primary amine in ethanol, an intractable condensation material is obtained after evaporating the solvents, but the ferrate-glutaraldehyde-amine system gives N-substituted piperidines: the ferrate acts as an efficient and highly selective reducing reagent to give the N-heterocycles as the only reaction products.^[9-15]

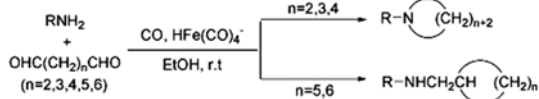


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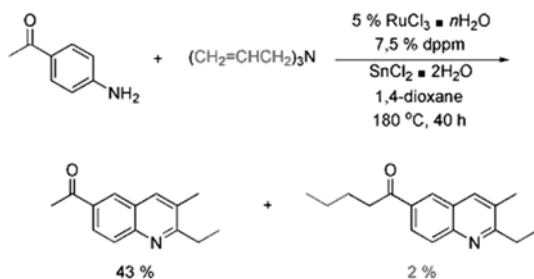
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According to the size of dialdehydes, azacyclization reaction was formed or not.

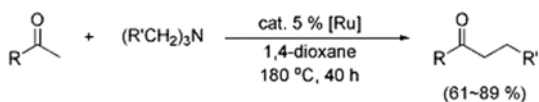


But when the ruthenium catalyst used, nine membered azacyclic compound can be formed.

For C-alkylation, we found unexpectedly that careful analysis of the crude reaction mixture revealed a small amount of 1-(2-ethyl-3-methylquinolin-6-yl)pentan-1-one (2%) in addition to the expected product 1-(2-ethyl-3-methylquinolin-6-yl)ethanone.^[16-19]

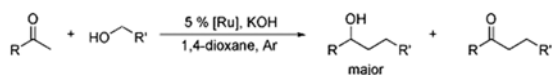


In this case, a new reaction, ruthenium-catalyzed regioselective α -alkylation of ketones: the *first* alkyl group transfer from trialkylamines to the α -C atom of ketones, was reported.^[20]



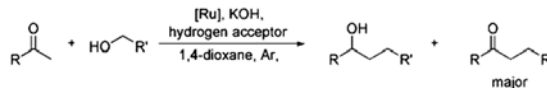
We have recently been engaged in ruthenium-catalyzed reactions and developed some novel reactions.

Prompted by these findings and intrigued by diverse reactivities of ruthenium catalysts, we have directed our attention to the transfer hydrogenation of ketones by alcohols only to discover the formation of unconventional transfer hydrogenation products. Here we are pleased to report our new findings.^[21]

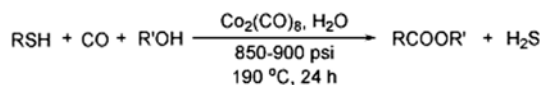


After changing the molar ratio of alcohol/ketone (from 3:1 to 1:1) in the presence of a hydrogen acceptor,

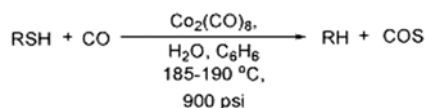
we can get alkylated ketone as the major product.^[22]



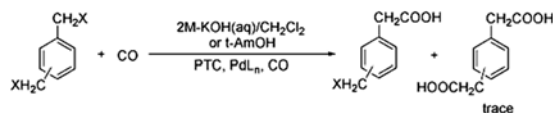
To our knowledge, no successful attempts to carbonylate mercaptans to esters have been reported in the primary or patent literature. In this case cobalt carbonyl can catalyze the desulfurization and carbonylation of mercaptans to carboxylic esters.



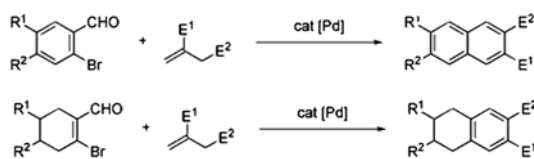
The role of water may be to induce disproportionation of cobalt carbonyl to the cobalt tetracarbonyl anion.^[23]



Various xylene dihalides could react with carbon monoxide in the presence of dibenzo-18-crown-6-ether or 18-crown-6-ether as a phase transfer agent and palladium (0) complex to afford the corresponding (halomethyl)phenylacetic acid in good yields and phenylenediacetic acid in trace amount under this two phase system, KOH(aq)/CH₂Cl₂ or t-amyl alcohol (org) at room temperature for 24 hours.



We have demonstrated that β -bromovinylaldehydes such as 2-bromobenzaldehydes and β -bromocyclohexene carboxaldehydes are coupled and cyclized with an array of functionalized alkenes in the presence of a catalytic amount of a palladium catalyst to give naphthalene and tetrahydronaphthalene derivatives in moderate to good yields.^[24-26]



It was suggested that the reaction proceeds via a sequence involving oxidation of alcohol to aldehyde and cross aldol reaction of aldehyde with ketone to form an α,β -unsaturated ketone which is subsequently hydrogenated to the initial oxidation of the starting alcohol. Prompted by these findings and intrigued by the diverse reactivities of ruthenium catalyst, we have directed our attention to the application of this methodology to the synthesis of N-heterocycles.^[27-31]



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