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Incorporation of CO and NO Ligands in the Reaction of Benzyl Bromides with Tetrabutylammonium Tricarbonylnitrosylferrate

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Reaction of benzyl bromides with tetrabutylammonium tricarbonylnitrosylferrate afforded N-benzylphenylacetamides via incorporation of CO and NO ligands accompanied with dibenzyl ketones. A noticeable substituent effect on the amide-forming reaction was observed.

Tetrabutylammonium tricarbonylnitrosylferrate (TBAFe) has been shown to be an useful reagent for the preparation of (η^3-allyl)Fe(CO)$_2$(NO) complexes.$^{1)}$ Although NO ligand generally remains intact in most reactions of nitrosyliron complexes, a few examples involving NO insertion into iron-carbon bond have been reported.$^{2-4)}$ During the investigation of the reaction of TBAFe with organic halides, we have found incorporation of CO and NO ligands in the reaction of TBAFe with benzyl bromides. We now report here a first example of amide-forming reaction incorporating NO ligand in the reaction of nitrosyliron complexes with benzyl bromides, and also a remarkable substituent effect on the insertion reaction of CO and NO.

$$\mathrm{ArCH_2X} + \underset{\text{TBAFe}}{\mathrm{Bu_4N[Fe(CO)_3(NO)]}} \longrightarrow \mathrm{ArCH_2CONHCH_2Ar} + \mathrm{(ArCH_2)_2CO} + \mathrm{(ArCH_2)_2}$$

A mixture of benzyl bromide (4.0 mmol) and TBAFe (2.0 mmol) in dichloromethane (20 ml) was stirred at 40 °C for 3 h under argon. After evaporation of the solvent, the residue was chromatographed on silica gel to give N-benzylphenylacetamide (dichloromethane : ethyl acetate=9 : 1) in moderate yield. The amide forming-reaction proceeded in the other solvents such as acetone, acetonitrile, and THF, and 1,2-dichloroethane. Dichloromethane is the most suitable solvent for the amide-forming reaction. The yields of the amides were independent of the reaction temperature in the range of 20 and 60 °C. The nitrogen atom of the amide arises from NO ligand of TBAFe via NO insertion into iron-carbon bonds. Among the reactions of carbonylnitrosyliron complexes, incorporation of NO ligand is a unique example. A few reactions have been hitherto reported with respect to NO insertion into iron-carbon bond.$^{2-4)}$

A remarkable substituent effect was observed on the CO and NO insertion reactions. Similar treatments of o- and p-methylbenzyl bromides with TBAFe also afforded the corresponding amides together with the corresponding dibenzyl ketones. On the other hand, electron withdrawing groups such as chloride and nitro group depressed the formation of the amides. The reaction of p-chlorobenzyl bromide gave the corresponding dibenzyl ketone as a main product, but the amide as a minor product. Further, the reaction of p-nitrobenzyl bromide resulted in the formation of 1,2-bis(p-nitrophenyl)ethane without incorporation of both CO and NO ligands. These results suggest that the NO insertion reaction exhibits electrophilic character.

Table 1. Reaction of Substituted Benzyl Halides with TBAFe

$ArCH_2X$	Yields/%[a]	
	Yield of amide	Others
$C_6H_5CH_2Cl$	2	Recovered $C_6H_5CH_2Cl$, 77
$C_6H_5CH_2Br$	68	$(C_6H_5CH_2)_2CO$, trace
$C_6H_5CH_2I$	63	$(C_6H_5CH_2)_2CO$, trace
o-$CH_3C_6H_4CH_2Br$	57	(o-$CH_3C_6H_4CH_2)_2CO$, 10
p-$CH_3C_6H_4CH_2Br$	59	(p-$CH_3C_6H_4CH_2)_2CO$, trace
p-$ClC_6H_4CH_2Br$	9	(p-$ClC_6H_4CH_2)_2CO$, 49
p-$NO_2C_6H_4CH_2Br$	0	(p-$NO_2C_6H_4CH_2)_2$, 49
1-(Bromomethyl)naphthalene	55	$(C_{10}H_7CH_2)_2CO$, trace

a) Isolated yields based on TBAFe used.

Davies et al.[5)] reported that the reaction of benzyl bromides with TBAFe in THF in the presence of CO, base, and methanol gave esters via CO insertion, but did not produce amides. The differences between the results of the present reaction and those of Davies are probably due to the reaction conditions. Chaudhari et al[6)] reported that alkyl halides reacted with Na[Fe(CO)$_3$(NO)] in the presence of triphenylphosphine to give acyliron complexes. However, reactions of alkyl bromides with TBAFe in the presence or absence of phosphine ligand were complex, giving no corresponding amides. In this amide-forming reaction, deoxygenation and hydrogenation of NO group take place. The hydrogen source is probably water contaminated in the solvent. The detailed mechanism is now under investigation.

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