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ADDITION OF METHYLENE CHLORIDE TO 1-OLEFINS ASSISTED BY DICHLOROBIS(TRIPHENYLPHOSPHINE)NICKEL(II)

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The reaction of methylene chloride with 1-olefins assisted by dichlorobis(triphenylphosphine)nickel(II) complex has been found to give 1:1 adducts in considerable yields.

Carbon tetrachloride and chloroform are known to react with olefins under the catalytic influence of iron,[1] copper,[1] or ruthenium[2] compounds to give 1:1 addition products. Methylene chloride, however, has not been reported to undergo such a reaction to our best knowledge. In this paper we wish to report the addition of methylene chloride to 1-olefins assisted by nickel-phosphine complexes, *e.g.*, dichlorobis(triphenylphosphine)nickel(II), to give 1:1 adducts.

$$CH_2Cl_2 + CH_2{=}CHR \xrightarrow[NiCl_2(PPh_3)_2]{} ClCH_2CH_2CHClR$$

Typically, into a stainless-steel autoclave equipped with an agitator were charged methylene chloride(180 mmol), 1-hexene(30 mmol), and dichlorobis(triphenylphosphine)nickel(II)(0.4 mmol) under nitrogen atmosphere. The autoclave was then heated to 150°C and contents were stirred for 20 h. The products were analyzed by glc.

Table 1 shows the catalytic influence of several group VIII metal complexes on the addition of methylene chloride to 1-hexene.

Table 1 Addition of CH_2Cl_2 to 1-hexene catalyzed by group VIII metal compounds[a)]

Catalyst	Yield of adduct(%)[b)]	Catalyst	Yield of adduct(%)[b)]
$NiCl_2(PPh_3)_2$	30	$NiCl_2(PPh_3)_2$	18[c)]
$RuCl_2(PPh_3)_3$	14	$NiCl(PPh_3)_3$	26[c,d)]
$PdCl_2(PPh_3)_2$	9	$Ni(PPh_3)_4$	trace[c)]
$RhCl(PPh_3)_3$	trace	$NiCl_2(n\text{-}Bu_3P)_2$	10[c)]
$CoCl_2(PPh_3)_2$	trace	$NiCl_2(Ph_2PCH_2CH_2PPh_2)$	1[c)]

a) 1-Hexene(15 mmol), CH_2Cl_2(75 mmol), catalyst(0.15 mmol); 140°C, 20 h.

b) Yields are based on the olefin charged(by glc). There are also produced 1-chloroheptane and 1,1,3-trichloroheptane though in much lesser amount. Isomerization of 1-hexene to 2-hexene is observed and addition products originated from 2-hexene have been detected.

c) 150 mmol of CH_2Cl_2 was used.

d) 0.75 mmol of $NiCl(PPh_3)_3$ was used.

Table 2 Addition of CH_2Cl_2 to 1-olefins catalyzed by $NiCl_2(PPh_3)_2$[a)]

Olefin	Product	Conversion(%)[b)]	Yield(%)[c)]
1-Pentene	$ClCH_2CH_2CHClC_3H_7$	37	19
1-Hexene	$ClCH_2CH_2CHClC_4H_9$	43	18
1-Hexene[d)]	$ClCH_2CH_2CHClC_4H_9$	59	35
4-Methyl-1-pentene	$ClCH_2CH_2CHClCH_2CH(CH_3)CH_3$	30	13
1-Octene	$ClCH_2CH_2CHClC_6H_{13}$	12	7

a) CH_2Cl_2(180 mmol), olefin(30 mmol), $NiCl_2(PPh_3)_2$(0.4 mmol); 150°C, 20 h.
b) Conversion was (moles of olefin consumed)/(moles of olefin charged).
c) Yields are based on the olefin charged. Small amounts of several by-products are also formed in every system.
d) 1.5 mmol of $NiCl_2(PPh_3)_2$ was used.

The nickel(I) and (II) complexes of triphenylphosphine are found to be effective for the addition reaction, whereas the nickel(0) complex shows scarecely any catalytic effect. The ruthenium(II) complex, which catalyzes effectively the addition of carbon tetrachloride and chloroform to 1-olefins is not so much effective for this reaction. Table 2 shows the results of the addition of methylene chloride to several 1-olefins assisted by dichlorobis(triphenylphosphine)nickel(II) complex. There seems to be a trend that a higher olefin gives the 1:1 adduct in somewhat low yield.

Although the mechanism of this reaction remains to be elucidated, our preliminary results may be rationalyzed by the following pathway by analogy with the previously suggested ones.[1,2)]

$$-\overset{|}{\underset{|}{Ni}}- + CH_2Cl_2 \longrightarrow -\overset{|}{\underset{|}{Ni}}-Cl + \cdot CH_2Cl$$

$$\cdot CH_2Cl + CH_2{=}CHR \longrightarrow ClCH_2CH_2\dot{C}HR$$

$$ClCH_2CH_2\dot{C}HR + -\overset{|}{\underset{|}{Ni}}-Cl \longrightarrow ClCH_2CH_2CHClR + -\overset{|}{\underset{|}{Ni}}-$$

This may be supported by the fact that the yield of the 1:1 adduct decreased to approximately one-half when a radical scavenger, 4-*t*-butylcatechol(ten fold excess to dichlorobis(triphenylphosphine)nickel(II)) was added to a 1-hexene system.

References

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