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REACTION OF *gem*-DIHALIDES WITH NICKEL(O) COMPLEXES: SELECTIVE METHYLENE INSERTION INTO C-H BOND OF OLEFINS

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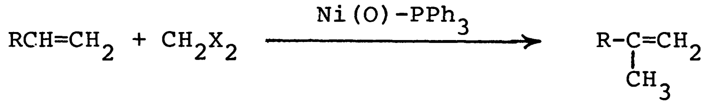
The reaction between methylene dihalides and ethylene assisted by the nickel(O)-triphenylphosphine complex has been found to give propylene, which was formed by selective methylene insertion into the olefinic C-H bond of ethylene. Similarly propylene and methylene dibromide gave isobutylene.

Activated *gem*-dihalides, R_2CX_2, such as dichlorodiphenylmethane and dibromoacetophenone are known[1)] to react with low valent transition metal complexes to give "the dimer" olefins, $R_2C{=}CR_2$, and/or "the cyclic trimers", cyclopropane derivatives. Recently we reported[2)] that a low valent nickel-2,2'-bipyridyl complex easily reacted at room temperature even with unactivated *gem*-dihalides such as methylene dihalides and ethylidene dihalides, yielding the corresponding olefins(eq. 1). During the course of studing ligand effects on the reaction between *gem*-dihalides and the nickel(O) complexes we found "the linear trimer", propylene, was produced from methylene dihalides when phosphines were employed as the ligand instead of 2,2'-bipyridyl(Bipy)(eq. 2). We now wish to report the first example of selective methylene insertion reaction into olefinic carbon-hydrogen bond.

$$2\ RCHX_2 \xrightarrow[\text{under } N_2]{\text{Ni(O)-Bipy}} \underset{R=H,\ CH_3}{RCH{=}CHR} \qquad \text{(eq. 1)}$$

$$3\ CH_2X_2 \xrightarrow[\text{under } N_2]{\text{Ni(O)-PPh}_3} CH_3CH{=}CH_2 \qquad \text{(eq. 2)}$$

The nickel(O)-triphenylphosphine complex reacted with methylene dibromide at room temperature under nitrogen atmosphere, giving propylene in 36% yield(based on methylene dibromide according to eq. 2) along with small amounts of ethylene and cyclopropane(Table 1). Excess of triphenylphosphine prevented the formation of propylene, and ethylene was formed as the major product. This may suggest that propylene was produced from the reaction of methylene dihalide with the intermediately formed ethylene. This assumption is supported by the following evidence. When the reaction was carried out under ethylene atmosphere(1 atm), the amount of propylene produced remarkably increased and *ca*. 0.5 mol of propylene was obtained from one mol of methylene dibromide. Thus, 2 mmol of bis(1,5-cyclooctadiene)nickel, $Ni(COD)_2$, and 4 mmol of PPh_3 were dissolved in oxygen free THF under ethylene atmosphere to give an orange yellow solution of $Ni(PPh_3)_2(CH_2{=}CH_2)$,[3] to which 2 mmol of CH_2Br_2 was added at once *via* syringe at 0°C. The mixture was stirred at that temperature for 0.5 hr and then allowed to react at room temperature, yielding the green solution of $Ni(PPh_3)_2Br_2$. The products were analyzed by V.P.C.. The



$$RCH{=}CH_2 + CH_2X_2 \xrightarrow{Ni(O)\text{-}PPh_3} R\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \qquad \text{(eq. 3)}$$

yields of propylene based on methylene dihalides are given in Table 2.

Cyclopropanes are formed from addition of carbenes or carbenoids to C=C bonds, as in Simmons-Smith reaction,[5] in which ethylene is converted to cyclopropane[6] by CH_2I_2 and Zn-Cu couple. The formation of propylene in the present reaction may involve transient formation of cyclopropane and its subsequent isomerization to propylene; there are some precedents for isomerization of cyclopropane effected by transition metal species.[7] From the reaction carried out in the presence of cyclopropane(run 8) cyclopropane was recovered quantitatively, the propylene yields being essentially the same regardless of the presence or absence of cyclopropane. This result implies that propylene is produced by the direct insertion of methylene into the C-H bond of ethylene. Addition to the C=C bond, in general, is the major reaction between carbenes or carbenoids and olefins with competing insertion into the C-H bonds,[8] and there seems to be no example of the selective insertion of methylene into olefinic C-H bonds.

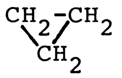
Similarly the reaction of propylene with methylene dibromide gave isobutylene along with small amounts of ethylene and butenes(Table 2, runs 28 and 29). The ethylidene group, CH_3CH, derived from ethylidene dibromide also inserted into the C-H bond of ethylene to give 1-butene. However, the product distribution was rather complicated due to the isomerization of 1-butene to 2-butene. The $Ni(O)\text{-}CH_2Br_2$ system was almost ineffective toward the methylene transfer to substituted ethylenes such as isobutylene and trans-2-butene.

The product distribution is strongly dependent on the nature of the donor ligand and its molar ratio to nickel(Tables 1 and 2). The highest yield of the methylene insertion product was obtained when the ratio PPh_3/Ni was 2. Increase in the ratio reduced the yield of propylene. This may suggest a pathway involving the reaction of methylene dibromide with ethylene coordinated on the nickel, because excess of triphenylphosphine prevents the coordination of ethylene to the

$$(Ph_3P)_2Ni(CH_2{=}CH_2) + n\ PPh_3 \longrightarrow (Ph_3P)_{2+n}Ni + CH_2{=}CH_2 \qquad \text{(eq. 4)}$$

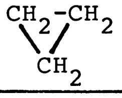
nickel(eq. 4). Low reactivities of substituted ethylenes may be ascribed to the instability of the π-olefin complexes with the low valent nickel.[9] The quite low yield of propylene in the system composed of bipyridyl as the ligand may be also understood by considering that there is no example in which ethylene is efficiently coordinated on the Bipy-nickel species.[10] The requirement of such

Table 1. Reaction of Methylene Dibromide with Ni(COD)$_2$-Donor under Nitrogen Atmosphere$^{a)}$

Run	Donor	Do/Ni$^{b)}$	Yield(%)$^{c)}$ of Product		
			$CH_2=CH_2$	$CH_3CH=CH_2$	
1	none	-	trace	0	0
2	Bipy	1	28	4	6
3	Bipy	2	46	trace	trace
4	Bipy	3	51	0	0
5	PPh_3	1	trace	34	trace
6	PPh_3	2	2	36	trace
7$^{d)}$	PPh_3	2	2	39	trace
8$^{e)}$	PPh_3	2	1	37	-
9	PPh_3	3	4	31	trace
10	PPh_3	4	19	25	0
11	PPh_3	5	25	4	0
12	PBu_3	2	14	0	0
13	$P(OPh)_3$	2	trace	0	0
14	$Ph_2PCH_2CH_2PPh_2$	1	22	2	0
15	$AsPh_3$	2	4	trace	0

a) Ni(COD)$_2$, 2mmol; solvent: THF 10 ml; room temperature for 5 hr; CH_2Br_2/Ni molar ratio, 0.9-1.0. b) Molar ratio of donor to nickel. c) Based on CH_2Br_2 according to eq. 2. d) Solvent: benzene 10ml. e) In the presence of 1 mmol of cyclopropane.

Table 2. Reaction of Methylene Dibromide with Ni(COD)$_2$-Donor under ethylene or propylene atmosphere$^{a)}$

Run	Olefin	Donor	Do/Ni	CH_2X_2	Solvent (ml)	Yield(%)$^{b)}$ of Product				
						$CH_2=CH_2$	$CH_3CH=CH_2$		$(CH_3)_2C=CH_2$	$C_4H_8$$^{c)}$
16	$CH_2=CH_2$	none	-	CH_2Br_2	THF(10)	-	0	0		
17	$CH_2=CH_2$	Bipy	1	CH_2Br_2	THF(10)	-	4	11		
18	$CH_2=CH_2$	Bipy	3	CH_2Br_2	THF(10)	-	4	5		
19	$CH_2=CH_2$	PPh_3	1	CH_2Br_2	THF(10)	-	41	3		
20	$CH_2=CH_2$	PPh_3	2	CH_2Br_2	THF(10)	-	43	2		
21	$CH_2=CH_2$	PPh_3	2	CH_2Br_2	THF(20)	-	56	trace		
22	$CH_2=CH_2$	PPh_3	2	CH_2Br_2	C_6H_6(10)	-	53	1		
23	$CH_2=CH_2$	PPh_3	3	CH_2Br_2	THF(10)	-	34	trace		
24	$CH_2=CH_2$	PPh_3	4	CH_2Br_2	THF(10)	-	10	trace		
25	$CH_2=CH_2$	PPh_3	5	CH_2Br_2	THF(10)	-	5	0		
26	$CH_2=CH_2$	PPh_3	2	CH_2I_2	THF(10)	-	47	6		
27	$CH_2=CH_2$	PPh_3	2	CH_2Cl_2	THF(10)	-	18	0		
28	$CH_3CH=CH_2$	PPh_3	2	CH_2Br_2	THF(10)	5	-		23	5
29	$CH_3CH=CH_2$	PPh_3	2	CH_2Br_2	C_6H_6(10)	4	-		28	7
30	$CH_3CH=CH_2$	PPh_3	4	CH_2Br_2	THF(10)	12	-		15	4

a) Reactions were carried out in 500 ml round bottle flask filled with olefin(1 atm). b) Based on CH_2X_2 according to eq. 3. c) Mixture of 1-butene, *trans*- and *cis*-2-butene with molar ratio of *ca.* 1:2:2.

coordination of olefin on the metal may suggest that the selective methylene insertion reaction would proceed through a hydridovinyl complex similar to that reported by Yamamoto et al.11) or an intermediate similar to that proposed in the reaction of the Ir-carbene complex with styrene.12)

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