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CYCLOPROPANATION OF ELECTRON-DEFICIENT OLEFINS WITH *gem*-DIBROMIDES CATALYZED BY NICKEL CATALYSTS

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The cyclopropanation of electron-deficient olefins with *gem*-dibromides was catalyzed by nickel catalysts. The addition of Lewis acids or sodium iodide and zinc resulted in an increase of the yield.

Zinc[1] and copper[2] are used as a catalyst for the cyclopropanation of olefins with *gem*-dihalides. In such a reaction electron-rich olefins are more reactive than electron-deficient ones. The cyclopropanation of electron-deficient olefins occurred with α-halo compounds by the copper-isonitrile complex,[3] and with diazo compounds by group VIII transition metal complexes.[4] We wish to report the cyclopropanation of electron-deficient olefins such as acrylonitrile (AN), methyl vinyl ketone (MVK), and methyl acrylate (MA) with *gem*-dibromides by nickel catalysts.

Methylene bromide (5 mmol) was added to a mixture of $Ni(PPh_3)_4$ (0.37 mmol), sodium iodide (6 mmol), zinc (8 mmol), and AN (10 mmol) in THF (10 ml). The reaction mixture was stirred at room temperature for 24h. Cyclopropanecarbonitrile was obtained in a 50% yield analyzed by GLPC of the distillate. Table I lists the cyclopropanation of electron-deficient olefins with methylene bromide catalyzed by Ni(0)-complexes in the presence of additives. AN or MA could not be cyclopropanated with methylene bromide using bis(1,5-cyclooctadiene)nickel, $Ni(COD)_2$, or $Ni(PPh_3)_4$ alone. Cyclopropane derivatives were formed from AN, MA, and MVK when bipyridyl (Bipy) or sodium iodide was added to $Ni(COD)_2$. Zinc was required for the cyclopropanation by $Ni(COD)_2$- or $Ni(PPh_3)_4$-Lewis acids systems. However, neither zinc nor Ni(0)-complexes-Zn systems had catalytic activity. The yields exceeded 100% based on Ni(0)-complexes in the presence of zinc. When nickel halides were reduced by zinc in the presence of ligands, Ni(0)-complexes were obtained accompanied by the formation of zinc halides. Instead of isolated Ni(0)-complexes as shown in Table I, we can use Ni(0)-complexes formed *in situ* from nickel halides, ligands, and zinc as catalysts without an addition of Lewis acids.

No cyclopropanation occurred with electron-rich olefins such as cyclohexene and vinyl ethers. It is worthwhile to note that no isomers were formed by these catalytic systems in contrast to the reaction of MA with diazomethane by $Ni(PPh_3)_4$.[4b] When MA was treated with CH_2I_2 and CH_2Br_2 by the catalysis of $NiBr_2(PPh_3)_2$-Zn at room temperature, the yields of methoxycarbonylcyclopropane were 18 and 73%, respectively. The yield, when the reaction of CH_2I_2 was carried out at 0°C, increased up to 52%.

Table I. Cyclopropanation of Electron-deficient Olefins with Methylene Bromide Catalyzed by Nickel Catalysts[a]

Olefin	Ni(0)-complex	mmol	Additive	mmol	Zn mmol	Yield[b] of cyclopropane derivative[c]	%
AN	Ni(COD)$_2$	0.87	Bipy	0.50	0	2.0	(12)
		0.59	NaI	4.0	0	6.7	(57)
		0.30	ZnBr$_2$	0.51	8	21	(180)
MA		0.64	NaI	4.0	0	13	(100)
		0.43	NaI	4.0	8	63	(740)
MVK		0.38	NaI	4.0	0	4.1	(55)
		0.65	NaI	4.0	8	39	(300)
AN	Ni(PPh$_3$)$_4$	0.37	NaI	6.0	8	50	(690)
MA		0.52	ZnCl$_2$	1.1	8	60	(440)
		0.30	ZnBr$_2$	0.15	8	75	(1200)
		0.27	ZnI$_2$	1.0	8	73	(950)
		0.31	AlCl$_3$	1.1	8	64	(1000)

a. A mixture of olefin (10 mmol), CH_2Br_2 (5 mmol), Ni(0)-complex, an additive, and zinc in THF (10 ml) was stirred at r. t. for 20-24h. b. GLPC yields based on CH_2Br_2. The number in parentheses is the yield based on Ni(0)-complexes. c. All products were identified by spectroscopic and elemental analyses.

When ethylidene bromide was treated with MA, MVK, and AN by the catalytic systems such as Zn- and $NiBr_2(PPh_3)_2$, $NiBr_2$-phenanthroline(phen)-NaI, and $NiBr_2$-PPh_3-phen-NaI, respectively, 2-methylcyclopropane derivatives were formed in isolated yields of 10% (cis:trans=2:3), 3.1% (1:4), and 1.7% (3:2).

Recently, nickel-carbenoid intermediates have been proposed from some evidence that the insertion of methylene into a nickel-ethyl group occurred in the reaction of $NiEt_2$(Bipy) and methylene chloride,[5] and cyclopropane was formed from that of ethylene and methylene bromide catalyzed by Ni(COD)$_2$ in the presence of Bipy.[6] This suggests that the cyclopropanation of AN with methylene bromide catalyzed by Ni(COD)$_2$ in the presence of Bipy or NaI as well as that of other electron-deficient olefins with *gem*-dibromides catalyzed by nickel complexes and zinc proceed *via* an intermediary nickel-carbenoid. A nucleophilic attack of the carbenoid on the electron-deficient olefins is suggested similar to the reaction of a tungsten carbenoid onto Michael acceptors.[7]

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