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CYCLO-COUPLING OF α,ω-DIHALOALKANES VIA OXIDATIVE ADDITION TO NICKEL(0) COMPLEX

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The nickel(0)-dipyridyl complex has been found to be a powerful reagent for preparing cycloalkanes from α,ω-dihaloalkanes. Dihalides, $Br(CH_2)_nBr$ n=3,4,5,6, gave cyclic products in high yields and dihalides, $X(CH_2)_nX$ n=1,2, X=Cl,Br, afforded ethylene.

Modern organic syntheses with organo transition metal complexes are the subject of great current interest. The generation of carbon-carbon bonds is accomplished, for instance, with organic halides and organo transition metal complexes.1) The cross-coupling reaction between organic halides and Grignard reagent with the nickel complex catalyst is one of the typical examples.2)

Reductive cyclization of α,ω-dihaloalkanes is a useful method of preparing cycloalkanes, and alkali metals, zinc, magnesium and chromium have been used as reducing agents,3) however most of them are limited to the closures of three membered rings. We previously reported4) that the systems consisting of di-Grignard reagents and transition metal halides gave cyclo-coupled products in good yields. Herein we wish to report that the nickel(0)-dipyridyl complex is a powerful reagent for preparing cycloalkanes from α,ω-dihaloalkanes.

It is well-known that low-valent nickel complexes are reactive species in oxidative addition of organic halides and useful reagents for the coupling of aryl and alkenyl halides.5) However, for cyclo-coupling of α,ω-dihaloalkanes the known systems containing nickel and donor ligands such as dimethylformamide and phosphines are not suitable because of their low reactivities and selectivities. For example, the reaction of 1,5-dibromopentane with the system containing $Ni(1,5\text{-}COD)_2$ and phosphines(PPh_3, PBu_3 or $Ph_2PCH_2CH_2PPh_2$) gave an isomeric mixture of C_5 hydrocarbons such as pentane, 1-pentene, cis- and trans-2-pentene, 1,4-pentadiene and cyclopentane. We have found α,α'-dipyridyl, which is known to be an excellent stabilizing ligand of the alkyl-transition metal bond,6) is the best donor ligand in the system, $Ni(COD)_2$-donor, for the purpose of preparing cycloalkanes from α,ω-dihaloalkanes. The results obtained from the present work are summarized in Table 1. The typical procedure is as follows. A mixture of $Ni(COD)_2$(2 mmol) and dipyridyl(6 mmol) was dissolved in 10 ml of oxygen free THF under nitrogen atmosphere, giving a violet blue solution. After 0.5 hr 1,5-dibromopentane(2 mmol) was added all at once via syringe into the solution at room

Table 1. Cyclo-coupling of α,ω-Dihaloalkanes with Ni(COD)$_2$-Dipyridyl[a]

Run	$Br(CH_2)_nBr$	Dipy/Ni[b]	$Br(CH_2)_nBr$/Ni[c]	Yield(%)[d] of Product		
				$(CH_2)_n$	$H(CH_2)_nH$	$H(CH_2)_{n-2}CH=CH_2$
1	$Br(CH_2)_2Br$	3	0.52	100[e]	0	-
2	$Br(CH_2)_2Br$	3	1.00	100[e]	0	-
3	$Br(CH_2)_3Br$	3	0.46	91	0	0
4	$Br(CH_2)_3Br$	3	0.98	78	0	0
5[f]	$Br(CH_2)_4Br$	3	0.48	52	0	trace
6	$Br(CH_2)_5Br$	1	0.44	64	0	1
7	$Br(CH_2)_5Br$	1	0.97	33	0	1
8	$Br(CH_2)_5Br$	2	0.52	80	0	1
9	$Br(CH_2)_5Br$	2	0.99	62	0	trace
10	$Br(CH_2)_5Br$	3	0.50	83	0	1
11	$Br(CH_2)_5Br$	3	0.93	83	0	1
12[f]	$Br(CH_2)_6Br$	3	0.50	52	trace	4
13[g]	$Br(CH_2)_6Br$	3	0.53	66	trace	trace
14[h]	$Br(CH_2)_5Br$	3	100	62	6	7

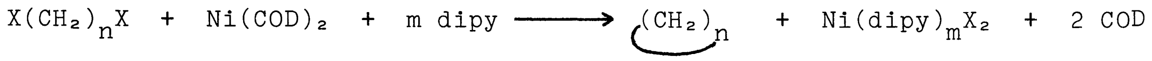
a) Ni(COD)$_2$, 2 mmol; solvent, THF 10 ml; room temperature for 5 hr.
b) Dipyridyl/Ni molar ratio. c) Dihalide/Ni molar ratio. d) The yields are based on dihalides. e) Ethylene. f) Decomposed with oxygen. g) Decomposed with acrylonitrile. h) Catalytic reaction using iso-C_3H_7MgBr(45 mmol) as reducing agent for Ni(II) to Ni(0); Ni(COD)$_2$, 0.2 mmol; THF, 50 ml.

Table 2. Coupling of Dihalomethane with Ni(COD)$_2$-Dipyridyl[a]

Run	CH_2X_2	CH_2X_2/Ni	Yield(%) of ethylene
15	CH_2Br_2	0.52	58
16	CH_2Br_2	∞[b]	41[c]
17	CH_2Cl_2	∞[b]	25[c]

a) Ni(COD)$_2$, 2 mmol; Dipy/Ni molar ratio, 3.
b) Dihalomethane(10 ml) was employed.
c) The yields are based on Ni(COD)$_2$.

temperature. The mixture was stirred at room temperature for 5 hr, yielding cyclopentane and Ni(dipy)$_3$Br$_2$. The outstanding feature of this reaction is the exclusive formation of cyclic products. Thus, 1,3-dibromopropane and 1,5-dibromopentane afforded cyclopropane and cyclopentane, respectively, in almost quantitative yields. 1,2-Dibromoethane similarly gave ethylene. Interestingly methylene halides such as methylene chloride and methylene bromide reacted smoothly at 0°C to give ethylene in moderate yields(Table 2).



$$X(CH_2)_nX + Ni(COD)_2 + m\ dipy \longrightarrow (CH_2)_n + Ni(dipy)_mX_2 + 2\ COD$$

1,4-Dibromobutane, however, directly gave no cyclobutane. The addition of the dibromide to the Ni(COD)$_2$-dipyridyl system(violet blue solution) produced a deep green solution which was stable at least up to 55°C and decomposed by oxygen to liberate cyclobutane in 52% yield. The similar phenomenon was also observed on 1,6-dibromohexane and in this case cyclohexane was produced by the action of oxygen, carbon monoxide or activated olefins like acrylonitrile[7] on the green solution. Treatment of the green solution with gaseous HCl generated n-alkane(n-butane or n-hexane) in a good yield, suggesting the existence of an alkyl nickel complex which resulted from oxidative addition of the dihalide to the nickel(0) species. Whereas in the case of 1,5-dibromopentane, the green color was observed for a short period and then disappeared with formation of cyclopentane. These phenomena imply that the cyclo-coupling reaction proceeds through an alkyl nickel intermediate which may have the structure similar either to metallocycles reported by Whitesides[8] and Grubbs[9] or to binuclear alkyl complexes prepared by Collman.[10]

The yield of the cyclic product strongly depends on the ratios of dipyridyl and the dihalide to nickel(Table 1, runs 6-11). In the absence of dipyridyl cyclopentane and other C$_5$ hydrocarbons were not formed at all. In the presence of one mole of dipyridyl per mole of nickel, less than 0.5 mole of the dihalide gave the cyclic product in a good yield, however use of one mole of the dihalide resulted in lowering the yield of the cyclic product. The best yield was obtained on employing 3 moles of dipyridyl per mole of nickel. Other donor ligands such as o-phenanthroline and tetramethylethylenediamine are also effective for the cyclo-coupling. As the solvents, THF, ether, dioxane, benzene, and acetone are useful, however alcohols such as methanol and ethanol can not be used because they afforded n-alkane as a major product. The reaction in EtOH gave n-pentane and cyclopentane in yields of 66% and 8%, respectively, and that in MeOH gave n-pentane in 65% yield as sole C$_5$ hydrocarbon product.

The potential application to organic syntheses would be expected since this cyclo-coupling reaction proceeds catalytically by the aid of an appropriate reducing agent for Ni(II) to Ni(0)(Table 1, run 14).

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