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MICHAEL ADDITIONS CATALYZED BY NICKEL(II) OR COBALT(II)ACETATE-2,2'-BIPYRIDINE COMPLEXES

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In the presence of nickel(II) or cobalt(II)acetate-2,2'-bipyridine complexes, α,β-unsaturated ketones, methyl acrylate, and acrylonitrile were found to react with nitromethane, malononitrile, and aniline at room temperature under neutral condition to afford addition products in good yields.

Michael reactions are carried out under strong basic or acidic conditions, and therefore the reactions under such drastic conditions have sometimes caused side reactions.[1] Saegusa et al. reported that Michael reactions were catalyzed by copper(I)-isocyanide complex under neutral condition, however, acceptor compounds in the reactions were limited, since dimerization reaction occurred.[2]

We have found that in the presence of Ni(II) or Co(II)acetate-2,2'-bipyridine(bpy) complexes, acceptor compounds such as α,β-unsaturated ketones, methyl acrylate, and acrylonitrile react smoothly with donor compounds such as nitromethane, malononitrile, and aniline to give the corresponding adducts in good yields under very mild conditions without dimerization according to the following scheme. Now, we wish to report the results in this paper.

$$\underset{\text{(acceptor)}}{\text{X-CH=CH-Y}} + \underset{\text{(donor)}}{\text{HZ}} \xrightarrow[\text{DMF, r.t.}]{\text{M(OAc)}_2\text{-bpy(1:1)}} \text{X-}\underset{\text{Z}}{\text{CH}}\text{-}\underset{\text{H}}{\text{CH}}\text{-Y}$$

M: Ni or Co

In a typical experiment, a solution of chalcone(0.50mmol) in nitromethane (2ml) were added to a dark green solution of Ni(II)acetate-bpy complex prepared by addition of bpy(0.080mmol) to a solution of anhydrous Ni(II)acetate(0.080mmol) in DMF(2ml). The reaction mixture was stirred for 18h at room temperature, and then extracted with ethyl acetate. The organic layer was washed with water and evaporated in vacuo to give a yellow oil which was purified by preparative TLC. Colorless crystals obtained were identified as 1,3-diphenyl-4-nitrobutane-1-one by the Mp, NMR, and IR. The isolated yield of the product was 82%.

In a similar manner, other addition reactions catalyzed by Ni(II) or Co(II)-bpy complexes were carried out and the results are summarized in Table 1.

Reactions of nitromethane with β-substituted acceptors(No.1-8) afforded 4-nitro-1-butanone derivaties and the yields were almost good. Methyl acrylate (No.9), β-unsubstituted acceptor, also reacted with nitromethane to give the adduct in 61% yield. All the reaction products described above were 1:1 adducts of acceptor and donor compounds. However, the reaction of malononitrile with acrylonitrile(No.10) gave 1:2 adduct (1,3,3,5-tetracyanopentane).

Table 1. Michael reactions in the presence of $Ni(OAc)_2$-bpy complex(1:1)

No	X-CH=CH-Y (acceptor) X	Y	HZ (donor)	Reaction time(h)	Yield(%)[a]	Mp(°C)(lit)
1	C_6H_5	COC_6H_5	CH_3NO_2	18	82	101-102(101-102)[3]
2	p-$NO_2C_6H_4$	COC_6H_5	CH_3NO_2	45	73	105-106[b]
3	C_6H_5	COC_6H_4-pNO_2	CH_3NO_2	18	87	98-99[b]
4	C_6H_5	COC_6H_4-p-Cl	CH_3NO_2	20	86	84-85(80)[4]
5	4-Py	COC_6H_5	CH_3NO_2	18	96[c]	116[b]
6	C_6H_5CH=CH	COC_6H_5	CH_3NO_2	42	38	85-87(83-84)[5]
7	C_6H_5	$COCH_3$	CH_3NO_2	110	27	101-102(97-98)[6]
8	C_6H_5	COC_6H_5	$C_6H_5NH_2$	114	84	175-176(171-172)[7]
9	H	$COOCH_3$	CH_3NO_2	44	61[c]	oil[b]
10	H	CN	$CH_2(CN)_2$	18	83[c]	90-91(91)[8]

a) Yields were determined by isolation (based on initial amount of the acceptor compounds).

b) Identified by elemental analysis or by MS.

c) Co(II)acetate-bpy complex(1:1) catalyst was used.

The yields of the reaction No.1 catalyzed by only 2,2'-bipyridine itself or Ni(II)acetate itself were 15% and 0% respectively under similar reaction conditions. However, the yield of the same reaction catalyzed by Ni(II)-bpy complex(1:1) catalyst was remarkably increased to 82%. Such enhanced catalytic effect of Ni(II)-bpy complex should be emphasized in comparison with that of Ni(II)-ethylenediamine(1:1) complex (yield:10%). The effect of bpy in other M(II)-bpy complex also appeared in Co(II)acetate but not in Zn(II) and Cu(II)acetates. It was assumed that the reaction proceeded through a coordination of the substrate to the Ni(II)-bpy complex, since the interaction between the complex and chalcone was observed by electronic absorption spectra shift of the complex (630 nm) to 620 nm, when the chalcone was added to a solution of the complex in DMF. Further studies on the reactions are now in progress.

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