

a) Reaction conditions: rt, 42 h, DMF. b) Complex: M(II): L = 1 : 1. c) Calculated from GLC analysis. d) In DMSO, 84%; HMPA, 78%; MeOH 6% (under similar reaction conditions).

as DMF or DMSO, was favorable for this catalytic reaction, while an alcohol such as MeOH was entirely inadequate. However, when the amount of the solvent used was in a large excess (*e.g.*, 10 ml), the product yield decreased apparently. In all the reactions, a large excess of nitromethane (4 ml) was employed; otherwise, the product yield was very poor, as will be described below. The results of the reactions with various complex catalysts are summarized in Table 1. According to the results shown in Table 1, the catalysis of the $\text{Ni}(\text{OAc})_2\text{-bpy}$ (1 : 1) complex is best. On the contrary, the $\text{Cu}(\text{II})$ or $\text{Zn}(\text{II})\text{-bpy}$ (1 : 1) complex shows extremely poor catalytic activity under similar reaction conditions. It is also observed that the Cl^- or NO_3^- anion is unfavorable as the counter ion of the complex catalyst as far as $\text{Ni}(\text{II})$ or $\text{Co}(\text{II})\text{-bpy}$ is concerned. The ligands of dim-bpy and phen may exert a steric effect on the reactions, and 6- NO_2 -phen has probably both steric and electronic effects (0%). Ethylenediamine is not effective as the ligand of the complex for this reaction (21%).

In order to examine this ligand effect further, the reactions of chalcone and nitromethane with some $\text{Ni}(\text{II})$ complex catalysts were followed over a period of 20 h by means of GLC analysis. The complexes employed were 16 mol% of $\text{Ni}(\text{OAc})_2\text{-bpy}$, $\text{Ni}(\text{OAc})_2\text{-(bpy)}_2$, $\text{Ni}(\text{OAc})_2\text{-en}$, and 8 mol% of $\text{Ni}(\text{OAc})_2\text{-bpy}$ to chalcone. The reaction conditions were similar to those shown in Table 1. The correlations of the reaction time with the product yields are shown in Fig. 1. The figure displays a feature of the catalytic reactions reasonably well. The $\text{Ni}(\text{II})\text{-(bpy)}_2$ complex, prepared by the addition of a two-fold mol quantity of bpy to the $\text{Ni}(\text{II})$ ion, accelerates the reaction in the first stage, but not in the later half. On the other hand, in the case of a low concentration of the $\text{Ni}(\text{II})\text{-bpy}$ (1 : 1) catalyst (8 mol%), the reaction is slow, but proceeds steadily throughout the reaction time. The reaction with $\text{Ni}(\text{II})\text{-bpy}$ (1 : 1) affords the product in an 80% yield for 20 h in Fig. 1 and in an 86% yield for 42 h (Table 1). In the reaction with $\text{Ni}(\text{II})\text{-en}$ (1 : 1), the yield of 20% is reached within just 20 h (Fig. 1), and a 21% yield within 42 h (Table 1). Therefore, the reaction time of 20 h seems to be generally enough for this

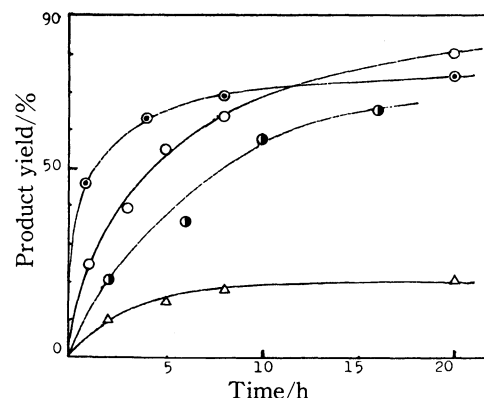


Fig. 1. Reaction profile of chalcone and nitromethane with $\text{Ni}(\text{II})$ complex catalysts (rt, in DMF).

○: $\text{Ni}(\text{II})\text{-bpy}$ (1 : 1); 16 mol% to chalcone, ◐: $\text{Ni}(\text{II})\text{-(bpy)}_2$ (1 : 2); 16 mol% to chalcone, △: $\text{Ni}(\text{II})\text{-en}$ (1 : 1); 16 mol% to chalcone, ●: $\text{Ni}(\text{II})\text{-bpy}$ (1 : 1), 8 mol% to chalcone.

complex-catalyzed Michael addition. It may be concluded that the $\text{Ni}(\text{OAc})_2\text{-bpy-DMF}$ system is the best combination for the complex-catalyzed Michael additions in this study. Some considerations of the enhanced effects of the bpy ligand and the OAc^- counter anion will be described below.

Various Michael Additions with the $\text{Ni}(\text{II})$ or $\text{Co}(\text{II})\text{-bpy}$ Complex.

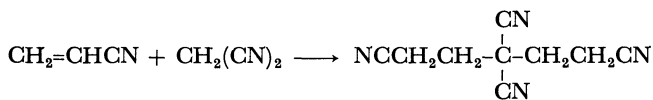
On the basis of the observations mentioned above, the reactions of various kinds of acceptor and donor compounds were carried out with the $\text{Ni}(\text{OAc})_2$ or $\text{Co}(\text{OAc})_2\text{-bpy}$ (1 : 1) complex in DMF. The reaction conditions were similar to those shown in Table 1 except for the reaction time. In these experiments, all the reaction products were isolated and determined; they were found to be 1 : 1 adducts of the donor and acceptor compounds, except for one case. No by-product was observed in any of the reactions. The results are summarized in Table 2. In general, $\text{Ni}(\text{II})$ and $\text{Co}(\text{II})$ ion species each seem to display their own individual characteristics. For instance, the $\text{Co}(\text{II})\text{-bpy}$ complex is almost inactive in Reaction No. 1 (66 h, 50%) as compared with $\text{Ni}(\text{II})\text{-bpy}$ (18 h, 82%), but it shows almost the same activity in Reactions

TABLE 2. VARIOUS MICHAEL ADDITIONS WITH $\text{Ni}(\text{II})$ OR $\text{Co}(\text{II})\text{-bpy}$ COMPLEX CATALYST^{a)}

No.	Acceptor (X-CH=CHCO-Y)		Donor (NM: CH_3NO_2)	Reaction time/h		Isolated yield/% ^{b)}	
	X	Y		Ni(II)	Co(II)	Ni(II)	Co(II)
1	Ph	Ph	NM	18	66	82	50
2	Ph	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4$	NM	18	15	87	88
3	Ph	<i>p</i> - ClC_6H_4	NM	20	42	86	86
4	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4$	Ph	NM	45	23	73	57
5	<i>p</i> - ClC_6H_4	Ph	NM	18	69	78	48
6	PhCH=CH	Ph	NM	42	—	38	—
7	Ph	Me	NM	100	—	27 ^{c)}	—
8	Ph	Ph	PhNH_2 ^{d)}	23	—	72	—
9	$\text{CH}_2=\text{CHCOOMe}$		NM	—	18	—	70
10	$\text{CH}_2=\text{CHCN}$		$\text{CH}_2(\text{CN})_2$	30	18	29	82 ^{e)}

a) Reaction conditions: $\text{M}(\text{II})\text{-bpy}$ (1 : 1), rt, in DMF. b) Reaction product: 1 : 1 adduct except for in No. 10. c) In the case of 50 °C, 90 h: 20%. d) A large excess to the acceptor. e) Crude.

No. 2 and No. 3. The influence of the electron-attractive substituents of chalcone (NO_2 , Cl) on the product yield are observed to some extent (Nos. 2 and 3). An inductive effect of the methyl group in the acceptor is observed in Reaction No. 7 (low reactivity). Reaction No. 9 with aniline did not proceed without the complex catalyst under these reaction conditions, although aniline itself might behave as a base catalyst. In the reaction of acrylonitrile with malononitrile, only 1,3,3,5-tetracyanopentane was obtained (No. 10). Besides the



reactions in the Table, the reactions of chalcone with acetophenone, *p*-nitroacetophenone, or dimethyl malonate were examined, but they did not proceed at all, not even at 80–100 °C. This complex-catalyzed Michael reaction seemed to be independent of the reaction temperature. When Reaction No. 7 was carried out at 50 °C for 90 h, the yield of the product was 20%, lower than that at room temperature, while Reaction No. 6 at 80 °C for 44 h gave a 37% yield (see Table 2).

Catalysis of the Metal(II) Complexes. With regard to the enhanced effect of the bpy ligand on the complex catalysis, several studies of other organic reactions have previously been reported.⁵⁾ According to their accounts, the net plus charge of the M(II) ion will increase upon the π -back donation of the M(II) ion to the bpy ligand in the complex; then, the resulting enhanced coordination force of the substrates to the M(II) ion will naturally accelerate the reactions. The ligand effects on the complex-catalyzed Michael reactions are also explainable by a similar π -back donation in the Ni(II) or Co(II)-bpy complexes. In the case of our study, no such reaction occurred with only the M(II) ion itself, but bpy complexes of the Ni(II) or Co(II) ion showed considerable catalytic activity. On the other hand, the ethylenediamine ligand with no π -back donation showed a very poor ligand effect on the complex catalysis.

In the course of the reaction, it is presumed that the substrates are activated by coordination to the M(II) ion of the complex catalysts. Therefore, the coordination of 4'-nitrochalcone to the Ni(II)-bpy complex was

examined by means of the electronic absorption spectra, as is shown in Fig. 2. A solution of $\text{Ni}(\text{OAc})_2$ in DMF showed an absorption maximum at 430 nm. When bpy was added to this solution (1 : 1), a new absorption maximum appeared at 630 nm which was attributed to the d-d band of Ni(II)-bpy chelation. When chalcone was added to this solution of the complex, the absorption maximum shifted to 620 nm. This fact might suggest that chalcone entered the first coordination sphere of the Ni(II) ion. Since no absorption shift was observed upon the addition of nitromethane to this complex solution, the interaction between the Ni(II) ion and nitromethane seemed to be extremely weak. Consequently, a high concentration of nitromethane (excess) might be required for satisfactory reactions. Therefore, in all the reactions shown in Tables 1 and 2, a large excess of nitromethane or other donors had to be employed. For example, in the reaction of chalcone and excess nitromethane (4 ml) with the Ni(II)-bpy complex, the yield of the product was 82% (Table 2, No. 1), but it decreased to 45% when an equimolar amount of nitromethane (1 mmol) was used under similar reaction conditions. On the other hand, if the coordination of chalcone is weakened or interrupted for some reason, the reaction will be very slow. According to the examination of some reaction solvents, MeOH was not suitable for the reaction (Table 1, footnote d). Therefore, the electronic absorption spectroscopy of this system was also carried out. A solution of the Ni(II)-bpy complex in MeOH showed an absorption maximum at 580 nm (Fig. 2). However, no shift of the absorption maximum was observed at all upon the addition of chalcone to this solution. This fact suggested that the coordination of chalcone to the Ni(II) ion was extremely weak or was interrupted by the stronger coordination of the methanol molecules. Actually, the yield of the reaction product in MeOH was only 6% for 42 h. The coordination of 4'-nitrochalcone was confirmed by the UV spectra, as above, and the yields in Reactions No. 2 and No. 3 (Table 2) were high. Therefore, it is presumed that the effects of electron-attractive groups in chalcone derivatives enhance their reactivity without any interruption of their coordination.

As for the behavior of the donor compound represented by nitromethane, it is considered that deprotonation occurs to form a donor anion in the first stage of the reaction; this process is also assisted by the metal complex. In our reaction system, the function of the M(II)-bpy complex catalyst as a base may be attributable not to the bpy ligand, but to the counter anion OAc^- , since bpy is not free because of the coordination in the complex. The IR spectra of $\text{Ni}(\text{OAc})_2$ showed an absorption maximum of OAc^- at 1500 cm^{-1} , but it shifted to 1560 cm^{-1} in the spectra of the $\text{Ni}(\text{OAc})_2$ -bpy complex, which suggested the location of OAc^- at the outersphere of the complex, as in the case of $[\text{Ni}(\text{II})\text{-bpy}](\text{OAc})_2$. Accordingly, both OAc^- and CH_3NO_2 are located considerably far from the central M(II) ion, although they have very weak interaction with the M(II) ion. In this situation, CH_3NO_2 may be catalyzed by OAc^- to form the CH_2NO_2^- anion. Thus, the dual role of the complex catalyst, the simultaneous

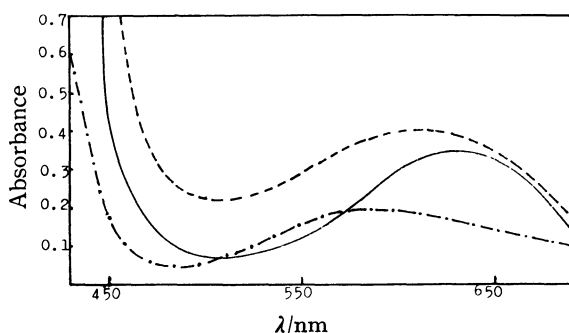


Fig. 2. Electronic absorption spectra of Ni(II)-bpy complexes in DMF or MeOH.

—: Ni(II)-bpy in DMF ($\lambda_{\text{max}}=630\text{ nm}$), ----: Ni(II)-bpy-4'-nitrochalcone ($\lambda_{\text{max}}=620\text{ nm}$), ·—·: Ni(II)-bpy in MeOH ($\lambda_{\text{max}}=580\text{ nm}$),: Ni(II)-bpy in DMF ($\lambda_{\text{max}}=430\text{ nm}$).

