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Michael Additions Catalyzed by Metal(II) Complexes

Ken-ichi WATANABE,* Ken-ichi MIYAZU, and Kazuo IRIE
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158

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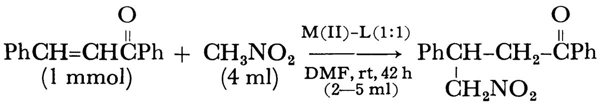
Michael-addition reactions have been found to proceed in the presence of the $Ni(OAc)_2$ or $Co(OAc)_2$–2,2′-bipyridine complex in DMF under neutral conditions at room temperature without any by-product. The reactions of chalcone and its derivatives with nitromethane generally gave good results. The effects of metal(II) ions, ligands, counter ions, and solvents on the catalysis were examined, and the features of the metal-complex-catalyzed Michael reactions were studied, with some considerations also being given to the catalysis mechanism.

Michael-addition reactions are generally carried out in the presence of strong base catalysts; reactions carried out under such drastic conditions have sometimes caused side reactions.[1] Recently, we have found that the reactions are catalyzed by the Ni(II) or Co(II)–2,2′-bipyridine(bpy) complex in DMF to afford addition products without any by-product; a brief note has already been reported.[2] With regard to Michael reactions catalyzed by metal complexes, Saegusa and his co-workers[3] employed the copper(I) isocyanate complex; however, acceptor compounds in the reactions were limited since the dimerization of olefins occurred. Nelson and his co-workers[4] employed the $Ni(acac)_2$ complex for the reaction of β-diketones with acceptor compounds, mainly α,β-unsaturated ketones. In this complex-catalyzed reaction, the complex catalyst and donor compounds are limited to $Ni(acac)_2$ and β-diketones, and the reactions are heterogeneous catalytic system in dioxane or dichloromethane. In our homogeneous catalytic system, for example, the reactions of α,β-unsaturated ketones with nitromethane proceed smoothly in the presence of the complex catalysts under neutral conditions at room temperature, without any by-product. The preparation of the complex catalysts is simple, the Michael reactions proceed under very mild conditions, and the reaction products are easily isolated in relatively pure form because there are no side reactions. The most important factors for the catalytic reactions are kinds of metal-ion species, ligands, counter ions of the complexes, and solvents. In this paper, the results of an examination of these factors and the scope and limitation of the complex-catalyzed Michael reactions will be described in detail; some considerations of the reaction mechanism will also be presented.

Results and Discussion

Effects of the Complex Catalysts. First of all, various kinds of metal complex catalysts were examined in the addition reaction of nitromethane to 1,3-diphenyl-2-propen-1-one(chalcone) in a DMF solvent. The reaction conditions are shown as follows:



$$\underset{\text{(1 mmol)}}{\mathrm{PhCH{=}CH\overset{\overset{O}{\|}}{C}Ph}} + \underset{\text{(4 ml)}}{\mathrm{CH_3NO_2}} \xrightarrow[\substack{\text{DMF, rt, 42 h}\\ \text{(2—5 ml)}}]{\text{M(II)-L(1:1)}} \mathrm{PhCH(CH_2NO_2)\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}Ph}$$

The metal-ion species (M(II)) employed for the reaction were Co(II), Ni(II), Cu(II), and Zn(II), while the ligands (L) were 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dim-bpy), 1,10-phenanthroline (phen), 6-nitro-1,10-phenanthroline (6-NO_2-phen), and ethylenediamine (en). Equimolar amounts of the metal(II) salt and the ligand compound were added to DMF; then the complex formation was observed by means of the color changes. This complex solution was subsequently used as a catalyst for the reaction without the isolation of the complex as a crystal form. The amount of the complex catalyst used for the reaction was 16 mol% of chalcone. The homogeneous reaction mixture was stirred for 42 h at room temperature. No by-products were formed in the reactions (examined by TLC, GLC, and isolation), the amount of chalcone consumed after the reaction was determined by means of GLC analysis; the yield of the reaction product was then calculated. The product was 1,3-diphenyl-4-nitro-1-butanone, which was further isolated and determined by means of mp, IR, and NMR. For example, in the reaction with the Ni(II)–bpy (1 : 1) complex, the yield of the product, as determined by GLC, was 86%, and the isolated yield was 82% (mp 100—101 °C). The details of the method of GLC analysis and the isolation of the product will be described in the Experimental section.

The reaction did not proceed with only metal(II) ions, without the ligand, but the ligand compounds themselves showed a weak catalytic activity; *e.g.*, bpy itself without the metal(II) ion afforded the product in a 15% yield (GLC) under similar reaction conditions. The reaction also did not proceed without any solvent (heterogeneous). An aprotic and polar solvent, such

TABLE 1. MICHAEL ADDITION OF NITROMETHANE TO CHALCONE WITH COMPLEX CATALYSTS[a)]

$M(II)X_2$[b)]	Ligand[b)]	Yield/%[c)]
$Co(OAc)_2$	bpy	34
$Ni(OAc)_2$	bpy	86[d)]
$Cu(OAc)_2$	bpy	2
$Zn(OAc)_2$	bpy	6
$CoCl_2\cdot6H_2O$	bpy	0
$Co(NO_3)_2\cdot6H_2O$	bpy	0
$NiCl_2\cdot6H_2O$	bpy	0
$Ni(NO_3)_2\cdot6H_2O$	bpy	0
$Ni(OAc)_2$	dim-bpy	65
$Ni(OAc)_2$	phen	37
$Ni(OAc)_2$	6-NO_2-phen	0
$Ni(OAc)_2$	en	21

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 catalytci 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 $Ni(OAc)_2$–bpy (1 : 1) complex is best. On the contrary, the Cu(II) or Zn(II)–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 Ni(II) or Co(II)–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 Ni(II) complex catalysts were followed over a period of 20 h by means of GLC analysis. The complexes employed were 16 mol% of $Ni(OAc)_2$–bpy, $Ni(OAc)_2$–$(bpy)_2$, $Ni(OAc)_2$–en, and 8 mol% of $Ni(OAc)_2$–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 Ni(II)–$(bpy)_2$ complex, prepared by the addition of a two-fold mol quantity of bpy to the Ni(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 Ni(II)–bpy (1 : 1) catalyst (8 mol%), the reaction is slow, but proceeds steadily throughout the reaction time. The reaction with Ni(II)–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 Ni(II)–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 complex-catalyzed Michael addition. It may be concluded that the $Ni(OAc)_2$–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.

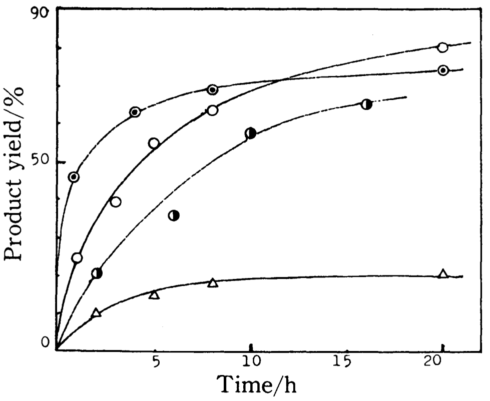


Fig. 1. Reaction profile of chalcone and nitromethane with Ni(II) complex catalysts (rt, in DMF).
○: Ni(II)–bpy(1 : 1); 16 mol% to chalcone, ⊙: (II)–$(bpy)_2$(1 : 2); 16 mol% to chalcone, △: Ni(II)–en(1 : 1); 16 mol% to chalcone, ◑: Ni(II)–bpy (1 : 1), 8 mol% to chalcone.

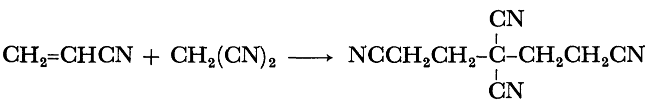
Various Michael Additions with the Ni(II) or Co(II)-bpy Complex. On the basis of the observations mntioned above, the reactions of various kinds of acceptor and donor compounds were carried out with the $Ni(OAc)_2$ or $Co(OAc)_2$–bpy (1 : 1) complex in DMF. The reaction conditions were similar to those 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, Ni(II) and Co(II) ion species each seem to display their own individual characteristics. For instance, the Co(II)–bpy complex is almost inactive in Reaction No. 1 (66 h, 50%) as compared with Ni(II)–bpy (18 h, 82%), but it shows almost the same activity in Reactions

Table 2. Various Michael additions with Ni(II) or Co(II)-bpy complex catalyst[a)]

No.	Acceptor (X-CH=CHCO–Y) X	Y	Donor (NM: CH_3NO_2)	Reaction time/h Ni(II)	Co(II)	Isolated yield/%[b)] Ni(II)	Co(II)
1	Ph	Ph	NM	18	66	82	50
2	Ph	p-$NO_2C_6H_4$	NM	18	15	87	88
3	Ph	p-ClC_6H_4	NM	20	42	86	86
4	p-$NO_2C_6H_4$	Ph	NM	45	23	73	57
5	p-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	CH_2=CHCOOMe		NM	—	18	—	70
10	CH_2=CHCN		$CH_2(CN)_2$	30	18	29	82[e)]

a) Reaction conditions: M(II)–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



$$CH_2{=}CHCN + CH_2(CN)_2 \longrightarrow NCCH_2CH_2\text{-}\underset{CN}{\overset{CN}{C}}\text{-}CH_2CH_2CN$$

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 $Ni(OAc)_2$ 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.

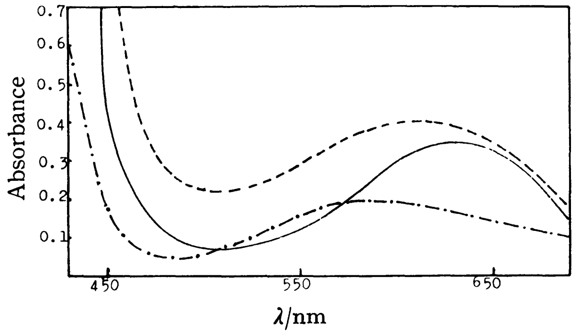
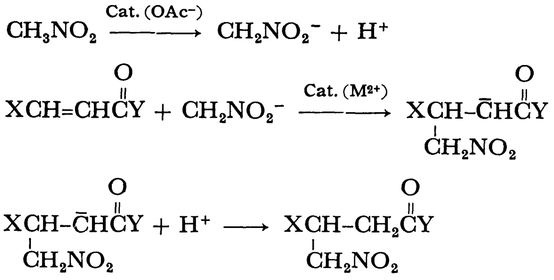


Fig. 2. Electronic absorption spectra of Ni(II)-bpy complexes in DMF or MeOH.
——: Ni(II)-bpy in DMF (λ_{max}=630 nm), ----: Ni(II)-bpy-4'-nitrochalcone (λ_{max}=620 nm), —·—·: Ni(II)-bpy in MeOH (λ_{max}=580 nm).

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 $Ni(OAc)_2$ showed an absorption maximum of OAc^- at 1500 cm^{-1}, but it shifted to 1560 cm^{-1} in the spectra of the $Ni(OAc)_2$-bpy complex, which suggested the location of OAc^- at the outersphere of the complex, as in the case of [Ni(II)-bpy] $(OAc)_2$. 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 activation of the acceptor by the M(II) ion and the donor by the OAc^- anion, should be emphasized.



$$CH_3NO_2 \xrightarrow{\text{Cat. }(OAc^-)} CH_2NO_2^- + H^+$$

$$XCH{=}CH\overset{O}{\overset{\|}{C}}Y + CH_2NO_2^- \xrightarrow{\text{Cat. }(M^{2+})} \underset{CH_2NO_2}{\underset{|}{XCH}}{-}\bar{C}H\overset{O}{\overset{\|}{C}}Y$$

$$\underset{CH_2NO_2}{\underset{|}{XCH}}{-}\bar{C}H\overset{O}{\overset{\|}{C}}Y + H^+ \longrightarrow \underset{CH_2NO_2}{\underset{|}{XCH}}{-}CH_2\overset{O}{\overset{\|}{C}}Y$$

Experimental

Instruments. The GLC analysis was carried out with a Hitachi K-53 gas chromatograph with a flame ionization detector, using a 1.0 m stainless steel tube column packed with 10% Carbowax 20 M on Diachrom A (career gas, N_2; injection temp, 240 °C; oven temp, 220 °C). The NMR and IR spectra were taken with a Hitachi Perkin-Elmer R-20 A spectrophotometer (60 MHz) and a Hitachi 215 Grating Infrared spectrophotometer respectively, the UV spectra, with a Hitachi EPS-3 T spectrophotometer.

Materials. The anhydrous metal(II) acetates were provided by Kojundo Chemical Research, and the hydrous metal(II) salts, by Wako Pure Chemicals. All the ligand compounds were provided by the Tokyo Kasei Co. Chalcone and its derivatives were prepared by aldol condensations with the Co(II)-bpy complex catalyst in DMF, according to the methods described in our previous report.[6] The other compounds in Table 2 were all commercially available.

Reactions of Chalcone and Nitromethane with Metal(II)-complex Catalysts (Tables 1 and 2). To a solution of metal(II) salt (0.16 mmol) in 2 ml of DMF, equimolar amounts of the ligand compound were added ($M^{2+}:L=1:1$). The color of the solution changed upon the complex formation. Then, 1 mmol of chalcone and 4 ml of nitromethane were added to the solution of the catalyst, after which the homogeneous reaction mixture was stirred for 42 h at room temperature. After the reaction, diethyl ether was added to the solution to precipitate the complex catalyst, and the supernatant was sampled for the GLC analysis (internal standard: α-(*p*-methoxyphenyl)acetophenone). Thus, the product yield was calculated from the quantity of chalcone unreacted, which was itself determined by comparing the relative peak area of chalcone *vs.* the internal standard with those shown in the calibration chart. The procedure for the isolation of the reaction product was that in which the reaction mixture was extracted with ethyl acetate, the organic layer was washed with water and then evaporated *in vacuo* to give a yellow oil. It was treated by the preparative TLC of silica gel (hexane–ethyl acetate), and the product was extracted with ethyl acetate and recrystallized with ethanol; 1,3-diphenyl-4-nitro-1-butanone, mp 100—101 °C (lit,[7] 101—102 °C), IR 1690 cm^{-1} (C=O), 1550 cm^{-1} (NO_2); ^1H-NMR ($CDCl_3$): δ 3.45 (d, 2H, CH_2–CO), 4.78 (d.d., 2H, CH_2–NO_2), 7.40—8.09 (m, aromatic).

Experiment for Fig. 1 (Reaction Profile). The reaction profile of chalcone and nitromethane with some complex catalysts was examined as follows: $Ni(OAc)_2$ and bpy (0.4 mmol each) were weighed in a volumetric flask (10 ml), DMF was added to the flask to dissolve the catalyst, and the solution was kept standing overnight at room temperature. Then, 2.5 mmol of chalcone and DMF were added to bring the flask up to the mark. The DMF solution (1 ml) was poured into each sample tube, and a further 1 ml of nitromethane was added to each sample tube. The reaction mixture was sampled from time to time, and a small quantity of methanol was added to a portion of the reaction mixture which was then stored in a freezer. The procedure of the GLC analysis of each sample was similar to that shown in Table 1.

UV Spectroscopy (Fig. 2). $Ni(OAc)_2$ (1.5 mmol) was dissolved in DMF (25 ml), and the UV spectra of this solution were measured. Then, to this solution 1.5 mmol of bpy was added and the UV spectra were measured again (absorption max., 630 nm). Next, 4′-nitrochalcone (0.6 mmol) was added to this complex solution, whereupon the absorption maximum was observed to shift to 620 nm. In the case of the methanol solvent, a similar procedure was carried out.

Reaction Products (Table 2). 1) As the forgoing. 2) Mp 98—99 °C; IR 1680 cm^{-1} (C=O), 1520 cm^{-1} (NO_2); ^1H-NMR ($CDCl_3$): δ 3.60 (d, 2H, CH_2–CO), 4.85 (d.d., 2H, CH_2–NO_2), 7.39—8.45 (m, aromatic). 3) Mp 82—84 °C (lit,[8] 80 °C); IR 1680 cm^{-1} (C=O), 1550 cm^{-1} (NO_2); ^1H-NMR ($CDCl_3$): δ 3.27 (d, 2H, CH_2–CO), 4.65 (d.d., 2H, CH_2–NO_2), 7.29—7.87 (m, aromatic). 4) Mp 105—106 °C; IR 1680 cm^{-1} (C=O), 1550 cm^{-1} (NO_2); ^1H-NMR ($CDCl_3$): δ 3.43 (d. 2H, CH_2–CO), 4.81 (d.d., 2H, CH_2–NO_2), 7.52—8.34 (m, aromatic). 5) Mp 97—98 °C; IR 1680 cm^{-1} (C=O), 1550 cm^{-1} (NO_2); ^1H-NMR ($CDCl_3$): δ 3.43 (d, 2H, CH_2–CO), 4.74 (d.d., 2H, CH_2–NO_2), 7.30—8.00 (m, aromatic). 6) Mp 85—87 °C (lit,[9] 83—84 °C); IR 1680 cm^{-1} (C=O), 1540 cm^{-1} (NO_2); ^1H-NMR ($CDCl_3$): δ 3.30 (d, 2H, CH_2–CO), 4.70 (d.d., 2H, CH_2–NO_2), 6.23 (d.d., 1H, =CH–), 6.73 (d, 1H, Ph–CH=), 7.40—8.18 (m, aromatic). 7) Mp 101—102 °C (lit,[10] 97—98 °C); IR 1720 cm^{-1} (C=O), 1550 cm^{-1} (NO_2); ^1H-NMR ($CDCl_3$): δ 2.11 (s, 3H, CH_3), 2.92 (d, 2H, CH_2–CO), 4.73 (d, 2H, CH_2–NO_2), 7.39 (s, aromatic). 8) Mp 175—176 °C (lit,[11] 171—172 °C). 9) Oil; IR (NaCl) 1730 cm^{-1} (COO), 1550 cm^{-1} (NO_2); ^1H-NMR ($CDCl_3$): δ 2.54 (4H, CH_2–CH_2), 3.76 (s, 3H, CH_3), 4.53 (t, 2H, CH_2–NO_2). 10) Mp 91—92 °C (lit,[12] 91 °C).

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