mmol Pd on the resin.

General Procedure of Hydrogenation. The hydrogenation was carried out in Brown Automatic Hydrogenator. The reaction flask, containing BER-Pd *in situ* prepared from BER (0.5 mmol in BH_4^-) and $PdCl_2$ (0.05 mmol) in 95% ethanol, was immersed in a water bath and maintained at 25℃ and then flushed with 1 *l* of hydrogen generated by injection of *ca.* 11 *ml* of sodium borohydride solution (1 M) into the hydrogen generator flask with stirring. The burette containing sodium borohydride solution (1 M) in 95% ethanol (stabilized with NaOH) was attached to hydrogen generator flask and then the height of the burette was adjusted to the position at which solution begins to flow just below or above the atmospheric pressure. To the reaction flask was added 10 mmol of substrate by syringe and then the reaction was initiated with stirring. The progress of hydrogenation was followed by measuring the volume of $NaBH_4$ solution used.

Hydrogenation of Aromatic Nitro Compounds over BER-Pd. Hydrogenation of 4-nitrophenol is representative. 1.391 g of nitrophenol (10 mmol) was added to the reaction flask containing 0.05 mmol of Pd on BER-Pd catalyst and hydrogenated at 25℃ and one atmospheric pressure. Hydrogenation ceased after three equiv. of hydrogen had been absorbed (90 min). Then the reaction mixture was filtered to remove the catalyst and solvent was removed on a rotary evaporator to give 1.04 g of 4-aminophenol (95% yield); mp. 186-188℃ (lit[11] 189.6-190.2℃).

Conclusions

1. Aromatic nitro compounds are selectively hydrogenated to the corresponding amines at room temperature and atmospheric pressure using BER-Pd catalyst without affecting other reducible groups also present, such as ketone, ether, ester, nitrile, chloro, benzyl alcohol, benzyl ether and benzylamino groups.

2. Aromatic nitro compound is selectively hydrogenated in the presence of aliphatic nitro compound.

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Synthesis and Radical Polymerization of *p*-(2,2,3,3-Tetracyanocyclopropyl)phenyl Acrylate and Methacrylate

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p-(2,2,3,3-Tetracyanocyclopropyl)phenyl acrylate (**3a**) and *p*-(2,2,3,3-tetracyanocyclopropyl)phenyl methacrylate (**3b**) were prepared by the reactions of bromomalononitrile with *p*-acryloyloxybenzylidenemalononitrile (**2a**) or *p*-methacryloyloxybenzylidenemalononitrile (**2b**), respectively. Compounds **3a** and **3b** were polymerized with free radical initiators to obtain the polymers with multicyano functionalities in the cyclopropane ring. The resulting polymer **4a** was soluble in acetone but the polymer **4b** was not soluble in common solvents. The inherent viscosities of polymers **4a** were in the range of 0.10-0.15 dL/g in acetone and those of **4b** were in the range of 0.20-0.30 dL/g in 98% sulfuric acid. Solution-cast films were cloudy and brittle, showing T_g values in the range of 106-125℃.

Introduction

Piezoelectric polymers have long been the subject of curiosity and have caused recent interest.[1] It is well-known that crystalline polymers having large dipole moment can exhibit piezoelectric effects if the main chains have all-planar zigzag

structure. The best known polymer is crystalline poly(vinylidene fluoride).[2] However, amorphous polymers with high concentrations of dipole moments can also exhibit the piezoelectric properties. The copolymer of vinylidene cyanide and vinyl acetate is such a case.[3]

Poly(acrylonitrile) has nitrile dipoles in high concentration, but the helical structure of the polymer main chain causes the radiating dipoles to cancel each other.[4] Introduction of a small amount (~5%) of comonomer can greatly increases the internal mobility of polymer segments. The copolymer of acrylonitrile with 7% methyl methacrylate does show piezoelectric behavior after stretching.[5] In the case of poly(1-bicyclobutanecarbonitrile), the rigid ring structure prevents helix formation and this polymer does indeed show piezoelectric behavior.[6]

A potentially piezoelectric polymer must contain a large concentration of dipoles and also be mechanically very strong. These polymers have to be film-forming and be able to withstand high voltages without breakdown. Unlike linear chains, in that the dipoles of vicinal cyano groups oppose each other, small rings hold vicinal cyano groups in roughly parallel alignment. Small rings, three- and four-membered, do not undergo large conformational changes which are found in the larger rings, most notably five- and six-membered rings. We have recently verified this concept by molecular modeling calculations and proposed that three- and four-membered rings with several cyano substituents held rigidly in alignment will have large dipole moments[7] and these polymers are potentially piezoelectric materials. We have previously prepared a series of polymers containing 1,1,2,2-tetracyanocyclopropane,[7,8] 1,1,2-tricyano-2-carbomethoxycyclopropane,[9,10] and 1,2-dicyano-1,2-dicarbomethoxycyclopropane units.[11]

This work is now extended to the synthesis of another polymer system containing multicyanocyclopropane rings. The present report describes the synthesis and radical polymerization of *p*-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate and methacrylate **3a-b**.

Experimental

Materials. The reagent grade chemicals were purified by distillation or recrystallization before use. *p*-Hydroxybenzaldehyde was crystallized from water containing a small amount of sulfuric acid and dried under vacuum. Acryloyl chloride and methacryloyl chloride (Aldrich) were distlled and used immediately. Triethylamine was refluxed over potassium hydroxide and distilled. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. 1,2-Dichloroethane and acetonitrile were refluxed with calcium hydride and fractionally distilled. Benzene was purified by refluxing over sodium metal, distilled, and stored over 4A molecular sieves under nitrogen. γ-Butyrolactone was dried with anhydrous calcium sulfate and distilled under nitrogen. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and stored at 5℃. Bromomalononitrile was prepared according to a literature procedure[12] and recrystallized twice from chloroform.

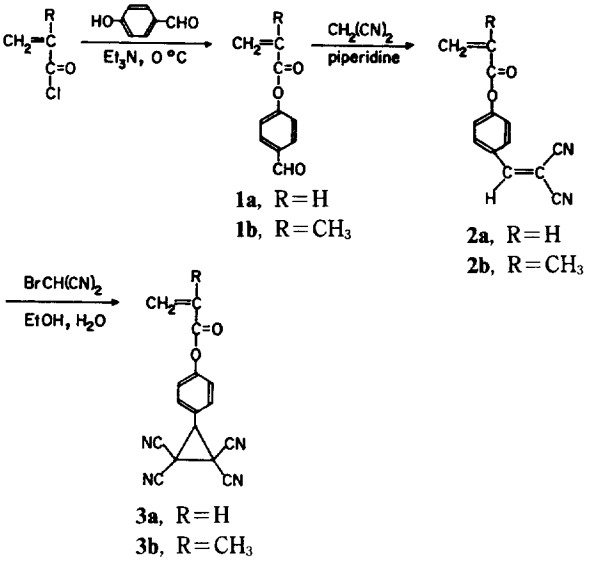
Measurements. IR spectra were taken on a Hitachi Model 260-30 infraraed spectrophotometer. ^{1}H-NMR spectra were obtained on a Varian 360 L NMR spectrometer (60 MHz). Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperatures (T_g) were measured on a DuPont 910 differential scanning calorimeter in nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10 ℃/min up to 700℃ was used for the thermal degradation study of polymers under nitrogen atmosphere. Melting points were measured in Buchi 512 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer. *p*-Acryloyloxybenzaldehyde (**1a**) and *p*-methacryloyloxybenzaldehyde (**1b**) were prepared by a published procedure.[11]

***p*-Acryloyloxybenzylidenemalononitrile (2a).** Piperidine (0.27 g, 3.2 mmol) was added to a solution of *p*-acryloyloxybenzaldehyde (5.28 g, 30 mmol) and malononitrile (1.98 g, 30 mmol) in 35 mL of *n*-butanol with stirring at room temperature. The resulting solution was stirred for 5 min at room temperature and 2 hr at 0℃. The product was filtered and washed with cold *n*-butanol, water containing a small amount of acetic acid, and cold *n*-butanol. The obtained white product was recrystallized from ethanol-acetone (80/20, vol/vol) mixtures to give 5.25 g (78% yield) of **2a**. Mp. 94-96℃, ^{1}H-NMR (acetone-d_6) δ 7.94-8.35 (t, 3H), 7.31-7.62 (d, 2H), 6.36-6.62 (m, 2H), 5.87-6.29 (m, 1H); IR (KBr) 2228 (CN), 1735 (C=O), 1585, 1565 (C=C) cm^{-1}. Anal. Calcd for $C_{13}H_8N_2O_2$: C, 69.64; H, 3.60; N, 12.49. Found: C, 69.75; H, 3.65; N, 12.43.

***p*-Methacryloyloxybenzylidenemalonoitrile (2b).** Piperidine (0.18 g, 2.1 mmol) was added to a solution of *p*-methacryloyloxybenzaldehyde (3.80 g, 20 mmol) and malononitrile (1.32 g, 20 mmol) in 20 mL of *n*-butanol with stirring at room temperature. The resulting solution was stirred for 5 min at room temperature and 1 hr at 0℃. The product was filtered and washed with cold *n*-butanol, water containing a small amount of acetic acid, cold *n*-butanol. The obtained white product was recrystallized from ethanol-acetone (80/20, vol/vol) mixtures to give 3.91 g (82% yield) of **2b**. Mp. 107-109℃, ^{1}H-NMR (acetone-d_6) δ 7.86-8.36 (t, 3H), 7.25-7.64 (m, 2H), 6.27 (s, 1H), 5.71-5.92 (m, 1H), 2.02 (s, 3H); IR (KBr) 2232 (CN), 1742 (C=O), 1592, 1567 (C=C) cm^{-1}. Anal. Calcd for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.78. Found: C, 70.66; H, 4.28; N, 11.72.

***p*-(2,2,3,3-Tetracyanocyclopropyl)phenyl acrylate (3a).** *p*-acryloyloxybenzylidenemalononitrile (1.35 g, 6 mmol) ad bromomalononitrile (1.30 g, 9 mmol) were dissolved in 20 mL of 85% aqueous ethanol at 0℃. After stirring for 5 hr at 0℃, the product was filtered and rinsed once with 20 mL of 85% aqueous ethanol and twice with 20 mL of cold ethanol. The obtained white crystals were recrystallized from ethanol-acetone (90/10, vol/vol) mixtures to give 1.12 g (65% yield) of **3a**. Mp. 150-152℃, ^{1}H-NMR (acetone-d_6) δ 7.76-8.10 (d, 2H), 7.23-7.82 (m, 2H), 6.32-6.61 (m, 2H), 5.89-6.30 (m, 1H), 4.96 (s, 1H); IR (KBr) 2274 (CN), 1742 (C=O), 1636, 1609 (C=C) cm^{-1}. Anal. Calcd for $C_{16}H_8N_4O_2$: C, 66.67; H, 2.80; N, 19.44. Found: C, 66.58; H, 2.82; N, 19.37.

***p*-(2,2,3,3-Tetracyanocyclopropyl)phenyl methacrylate (3b).** *p*-Methacryloyloxybenzylidenemalononitrile (1.91 g, 8 mmol) ad bromomalononitrile (1.74 g, 12 mmol) were dissolved in 25 mL of 85% aqueous ethanol at 0℃. The resulting solution was stirred for 4 hr at 0℃. The product was filtered and rinsed once with 20 mL of 85% aqueous ethanol and twice with 25 mL of cold ethanol. The obtained white crystals



Scheme 1.

were recrystallized from ethanol-acetone (90/10, vol/vol) mixtures to give 1.69 g (70% yield) of **3b**. Mp. 158-160℃ (dec). ^{1}H-NMR (acetone-d_6) δ 7.86-8.36 (t, 3H), 7.25-7.64 (m, 2H), 6.27 (s, 1H), 5.71-5.92 (m, 1H), 2.02 (s, 3H); IR (KBr) 2232 (CN), 1742 (C=O), 1592, 1567 (C=C) cm^{-1}. Anal. Calcd for $C_{17}H_{10}N_4O_2$: C, 67.55; H, 3.33; N, 18.53. Found: C, 67.64; H, 3.30; N, 18.59.

Radical Polymerization of 3. A representative polymerization procedure (the case of **3a**) was as follows: A γ-butyrolactone (3.0 mL) solution of **3a** (0.86 g, 3 mmol) was placed in a polymerization tube, and 4.4 mg (2.7×10^{-4} mol) of AIBN was added under nitrogen. The mixture was degassed by freeze-thaw process under vacuum. After the mixture was warm to room temperature, it was placed in an oil bath kept at 65℃. After 12 hr, the polymerization tube was opened and the viscous product was poured into 400 mL of methanol. The precipitated polymer was collected and reprecipitated from acetone into methanol. The obtained polymer **4a** was dried in a vacuum oven at 30℃. **4a**: 0.39 g (45% yield); η_{inh}=0.15 dL/g (0.5 g/dL in acetone at 25℃). ^{1}H-NMR (acetone-d_6) δ 7.55-8.28 (m, 2H), 6.90-7.55 (m, 2H), 4.85 (s, 1H), 2.68-3.78 (m, 3H); IR 2260 (CN), 1755 (C=O), 1605 (C=C) cm^{-1}. Anal. Calcd for $(C_{16}H_8N_4O_2)_n$: C, 66.67; H, 2.80; N, 19.44. Found: C, 66.75; H, 2.83; N, 19.50. **4b**: 0.83 g (92 yield); η_{inh}=0.22 dL/g (0.5 g/dL in 98%-sulfuric acid at 25℃) IR (KBr) 2260 (CN), 1750 (C=O), 1603 (C=C) cm^{-1}. Anal. Calcd for $(C_{17}H_{10}N_4O_2)_n$: C, 67.55; H, 3.33; N, 18.53. Found: C, 67.65; H, 3.40; N, 18.62.

Results and Discussion

Synthesis of Monomers 3a-b. *p*-Acryloyloxybenzaldehyde (**1a**) and *p*-methacryloyloxybenzaldehyde (**1b**) were prepared by the well-known Schotten-Baumann method. *p*-Acryloyloxybenzylidenemalononitrile (**2a**) and *p*-methacryloyloxybenzylidenemalononitrile (**2b**) were prepared by the condensation of malononitrile with **1a** or **1b**, resepectively.[13] *p*-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate (**3a**) and *p*-(2,2,3,3-tetracyanocyclopropyl)phenyl methacrylate (**3b**) were synthesized by cyclopropane formation from bromomalononitrile and **2a** or **2b**, according to a variation of the Wideqvist reaction.[14] In 85% aqueous ethanol solution at 0℃, monomer **3a** and **3b** were obtained in 65-70% yields. The chemical structure of the compounds was confirmed by ^{1}H-NMR (Figures 1 and 2), IR spectra, and elemental analyses.

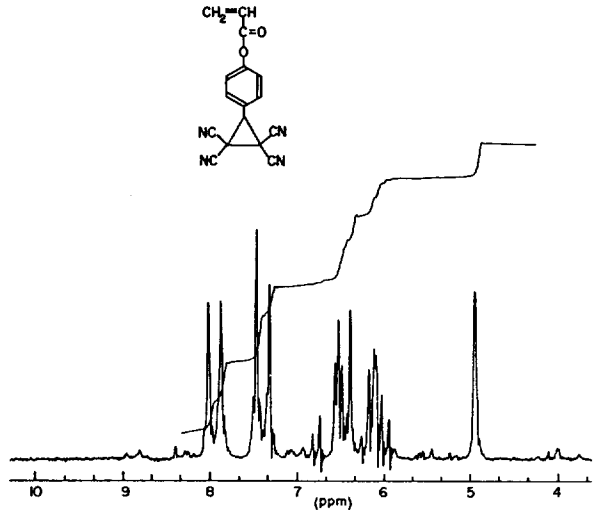


Figure 1. 60 MHz ^{1}H-NMR spectrum of *p*-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate (**3a**) taken in acetone-d_6 at room temperature.

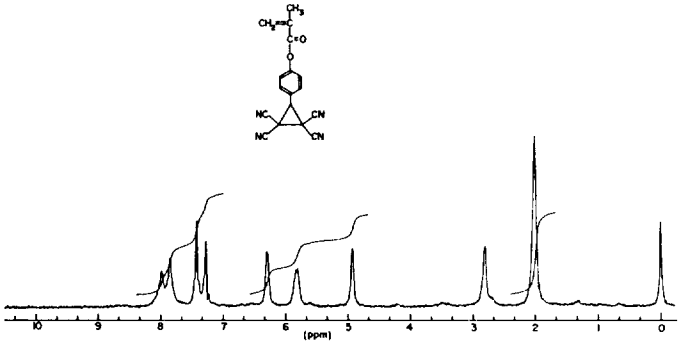


Figure 2. 60 MHz ^{1}H-NMR spectrum of *p*-(2,2,3,3-tetracyanocyclopropyl)phenyl methacrylate (**3b**) taken in acetone-d_6 at room temperature.

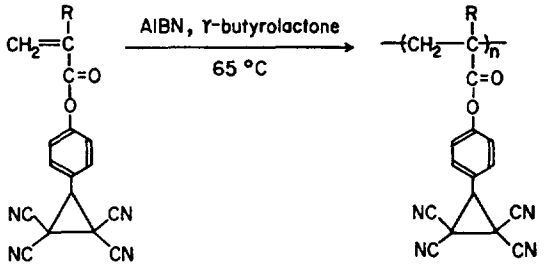
Radical Polymerization of Monomers 3a-b. Monomer **3a** and **3b** were polymerized by free radical mechanism using AIBN as initiator to obtain the polymers **4a-b** with multicyanocyclopropane groups. Polymerizations were carried out in solution at 65℃. The polymerization results are summarized in Table 1. The radical polymerizability of monomer **3a** was much lower than that of **3b** and yields of polymer **4a** were always lower than those of polymer **4b**, as shown in Table 1. The free radical initiator did not attack the cyclopropane ring during polymerization.

The chemical structure of the polymers **4a** and **4b** confirmed by ^{1}H-NMR (Figure 3), IR (Figure 4) spectra, and elemental analyses. Polymer **4a** was soluble in acetone but was not soluble in diethyl ether and chloroform. However, polymer **4b** was not soluble in acetone or in any other solvents except concentrated sulfuric acid. The polymer **4b** only swelled even when heated above 100℃ in strong solvents such as DMSO and DMF. The inherent viscosities of poly-

Table 1. Free Radical Polymerization of 3[a] by AIBN[b] at 65℃

Monomer	Solvent (vol/vol)	Wt. of monomer / vol of solvent in g/mL	Time in h	Conversion in %	η_{inh} in dL/g
3a	γ-butyrolactone	0.29	12	45	0.15[c]
3a	γ-butyrolactone	0.40	15	50	0.20[c]
3a	γ-butyrolactone	0.25	10	42	0.18[c]
3a	CH_3CN/C_6H_6, 2.0	0.32	12	40	0.14[c]
3b	γ-butyrolactone	0.32	12	92	0.22[d]
3b	γ-butyrolactone	0.40	15	95	0.27[d]
3b	γ-butyrolactone	0.25	10	90	0.25[d]
3b	CH_3CN/C_6H_6, 2.0	0.25	12	88	0.24[d]

[a] **3a**=*p*-(2,2,3,3-Tetracyanocyclopropyl)phenyl acrylate; **3b**=*p*-(2,2,3,3-Tetracyanocyclopropyl)phenyl methacrylate. [b] Concentration: 0.9 mol%. [c] Concentration: 0.5 g/dL in acetone at 25℃. [d] Concentration: 0.5 g/dL in 98%-sulfuric acid at 25℃.



3a, R=H
3b, R=CH_3

4b, R=H
4b, R=CH_3

Scheme 2.

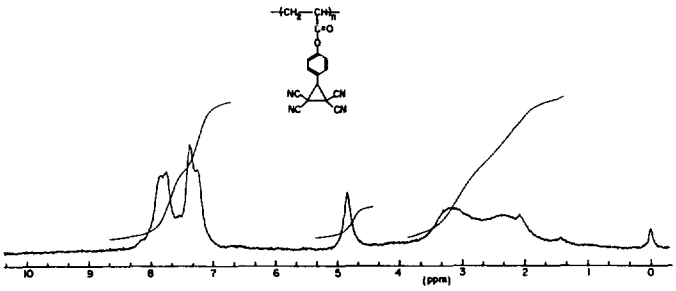


Figure 3. 60 MHz ^{1}H-NMR spectrum of polymer **4a** taken in acetone-d_6 at room temperature.

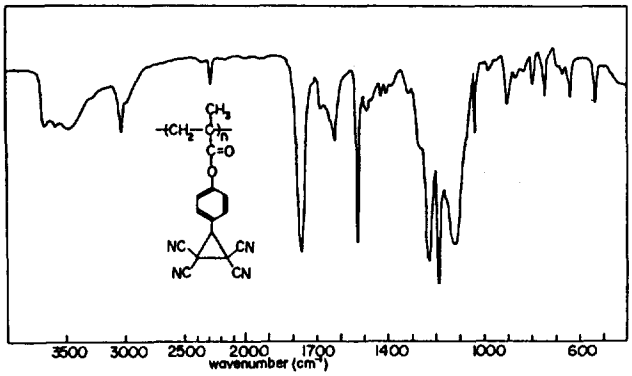


Figure 4. IR spectrum of polymer **4b**.

Table 2. Thermal Properties of Polymer **4**

Polymer	T_g[a] in ℃	Degradation temp in ℃[b] 5%-loss	20%-loss	40%-loss	Residue[b] at 700℃ in wt%
4a	105	350	403	567	32.0
4b	125	279	395	538	28.4

[a] Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10℃/min in N_2 atmosphere. [b] Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10℃/min in N_2 atmosphere.

mers **4a** were in the range of 0.10-0.15 dL/g in acetone and those of **4b** were in the range of 0.20-0.30 in 98% sulfuric acid. To examine the possibility of degradation of polymer **4b** in 98% sulfuric acid, viscosity of solution was measured at certain time interval for five days. However, no notable change in viscosity was observed. Another observation to note is that polymer **4b** was not recovered by reprecipitation from sulfuric acid into water. These observations indicate that the polymer **4b** undergoes extensive degradation during the process of dissolution in sulfuric acid.

The thermal behavior of the polymers were investigated by theromogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g) and the results are summarized in Table 2. The polymers show a double phase degradation pattern in their TGA thermograms, probably due to the presence of two rings in the pendant group. The T_g values were found to be about 120℃ for both polymers. These T_g values were higher than those of poly(methyl acrylate) (10℃) and comparable to those of poly(methyl methacryalte) (105℃). Films cast from polymer **4a** solution in acetone were brittle, and therefore the piezoelectric activity has not yet to be measured.

Conclusion

We prepared two new monomers **3a** and **3b** containing four cyano groups in a small cyclopropane ring. The tetra-

cyanocyclopropane-substituted acrylate and methacrylate compounds were polymerized radically to obtain the polymers with multicyano functions. Monomer **3b** was more reactive than **3a** toward free radical initiators and monomer **3b** polymerized readily in high conversion. The resulting substituted polyacrylate **4a** was soluble in acetone but was not soluble in chloroform or diethyl ether. However, tetracyao-substituted polymethacrylate **4b** was not soluble in common solvents. The T_g value of the polymer was around 120℃. Films cast from polymer **4a** solution were brittle, which could be due to the rather low molecular weights, as indicated by the inherent viscosities, and/or to the presence of strong dipoles in the side chain.

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Hydroiminoacylation of α,ω-diene with Aldimine by Rh(I) and Isomerization of the Terminal Olefin to the Internal Olefin

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Catalytic iminohydroacylation has been achieved by the reaction of aldimine **1** and 1,5-hexadiene (**2a**) with Wilkinson's complex as catalyst. Compounds **7a**, **8a** and **9a** were obtained as final product after hydrolysis of the resulting iminohydroacylation products **4a**, **5a** and **6a**. Depending on the reactant ratio (**2/1**), the ratio of products were changed dramatically : As the **2/1** ratio was increased, **7a** is the major product after hydrolysis while **8a** is the major with an 1/1 ratio of **2/1**. The mechanism of the formation of **5a** is determined by the reaction of **1** and **2b** under the identical reaction conditions. Considering that **5a** may not be formed from the hydroiminoacylation of **14a** since **5b** cannot be formed from that of conjugate diene **14b** generated from isomerization of **2b**, **5a** must be formed from the reaction of **4a** and **10** by addition-elimination mechanism.

Introduction

The activation of the C-H bond by transition metal complexes has received much interest in organometallic chemistry[1]. The C-H bond of aldehyde can be easily cleaved by transition metals such as Wilkinson's complex[2]. Subsequent decarbonylation of the acylmetal hydride and reductive elimination of the resulting alkyl metal hydride gives alkane[3]. This decarbonylation can be prevented by cyclometallation using specially modified substrate such as 8-quinolinecarboxaldehyde, since a five-membered ring is the right size for a stable metallacycle complex[4]. The terminal olefins undergo hydroacylation with 8-quinolinecarboxaldehyde to give alkyl 8-quinolinyl ketone under Rh(I) catalyst. However 8-quinolinyl group used for a hydroacylation tool is hard to be discarded in order to apply for the general ketone synthesis from aldehyde. For this purpose 2-aminopicolinyl group of aldimine **1** has been used for the hydroacylation tool which can be easily discarded by hydrolysis after the reaction[5]. It has been reported that the terminal olefin can be hydroiminoacylated catalytically or stoichiometrically with aldimine **1** on the rhodium(I) complex to give ketimine, which can be hydrolyzed to give corresponding ketone[5a]. Aldimine **1** also had been reacted with conjugate diene stoichiometrically