



Hydroesterification of 2-vinyl-6-methoxynaphthalene using palladium complexes containing chelating nitrogen ligands

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ABSTRACT

Hydroesterification of 2-vinyl-6-methoxynaphthalene (VMN) to methyl ester of 6-methoxy naphthyl propionic acid (ester of naproxen) has been investigated using palladium complexes containing the chelating N^oO and N^oN ligands (pyridine-2-carboxylate, 2-acetylpyridine, 2-pyridine-carboxaldehyde, and bipyridine) as catalysts. Palladium complex containing 2-acetylpyridine as the ligand was found to be superior to other Pd-complexes. Both acid and halide promoters were necessary for high activity and selectivity. As an acid promoter, benzenesulfonic acid was found to be more effective compared to *p*-toluenesulfonic acid. Formation of ether 2-methoxy-6-(1-methoxyethyl)naphthalene and a polymer of VMN was observed in all the reactions. It was observed that active catalytic species generated during carbonylation reaction was responsible for the polymer formation. The effect of various parameters such as solvents, CO pressure, and alcohols on the catalytic activity as well as the selectivity was investigated. The turnover frequency using the complex Pd(acpy)(PPh₃)(OTs)₂ (acpy = 2-acetylpyridine) catalyst was found to be 42 h⁻¹, which is the highest for the hydroesterification of VMN.

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1. Introduction

The transition metal complex catalyzed hydroesterification of olefins with CO and alcohol is of significant interest for the synthesis of linear fatty acid esters and branched 2-arylpropionic acid esters. Branched arylpropionic acid esters are industrially important as anti-inflammatory agents [1]. Various catalysts used for hydroesterification of olefins are cobalt [2] and palladium [3] compounds. The synthesis of esters with Pd catalysts requires relatively lower temperatures (50–125 °C) as compared to cobalt catalysts (>140 °C). However, mixtures of regio-isomers are often obtained and higher CO pressure (100 atm) is required [4]. Recently, improved palladium catalysts have been developed which are effective at relatively low pressures and selective for the generation of branched esters. Jayasree et al. [5,6] have proposed catalyst system comprising of Pd(pyca)(PPh₃)(OTs) complex and TsOH and LiCl promoters, for the carbonylation of a variety of olefins and alcohols. This catalyst system showed significant advancement (TOF~2600 h⁻¹ for hydroxycarbonylation of styrene) in low pressure catalytic carbonylation ($P_{CO} \sim 5.4$ MPa, 388 K) reactions. Seayad et al. [7] reported

the hydrocarboxylation of various olefins using PdCl₂(PPh₃)₂ as a catalyst along with TsOH and LiCl as promoters in which hydrocarboxylation of VMN is also demonstrated as one of the examples. However, there are only a few reports on the hydroesterification of important substrates such as VMN to the esters of naproxen and there is no information on the detailed parametric effects and quantitative details of the catalytic activity and selectivity. The catalytic systems reported for the hydroesterification of VMN include PdCl₂(MDPP)₂ [8] (MDPP = menthyl-diphenylphosphine) and silica-supported chitosan-palladium complex (CS-PdCl₂/SiO₂) [9], which showed very low turnover frequencies (<10 h⁻¹). There are also reports on asymmetric hydroesterification of VMN in which Hiyama and co-workers [10] have used dicycloalkylphosphinobinaphthalene as a chiral ligand along with PdCl₂, to show 53% enantioselectivity. This reaction was carried in the absence of acid promoters and high yields were obtained only after prolonged reaction times (24–144 h). Inoue and co-workers [11] described asymmetric hydroesterification using Pd(OAc)₂/(S)-(R)-BPPFA/*p*-toluenesulfonic acid as the catalytic system ((S)-(R)-BPPFA = (S)-1-[(R)-1',2-bis(diphenylphosphino)ferrocenyl]ethylenediamine). The reaction was carried out at room temperature for a period of 24 h, however, the reaction gave very poor conversions (~13%) with three products consisting of a branched ester, linear ester and ether (formed by the reaction of starting olefin and methanol catalyzed by acid). It is evident from these reports that the activity of Pd catalysts for

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hydroesterification of VMN is significantly lower than that of styrene and more detailed study on the role of catalyst precursors and promoters is necessary to explore improved catalysts with high activity and regio-selectivity. Herein we report hydroesterification of VMN using palladium complex catalysts having one hemi-labile chelating ligand as catalyst precursors. Effect of various reaction conditions on the activity and selectivity has been investigated.

2. Experimental

2.1. Materials

$\text{Pd}(\text{OAc})_2$, 2-acetylpyridine (acpy), pyridine-2-carboxylic acid (pyca), 2,2'-bipyridyl (bipy), pyridine-2-carboxaldehyde (pycald), triphenylphosphine, *p*-toluenesulfonic acid, benzenesulfonic acid, methanesulfonic acid, trifloromethanesulfonic acid, trifluoroacetic acid, lithium chloride, methanol, 4-*tert*-butylcatechol and CO (Matheson, USA) were used as-received without further purification. Solvents and alcohols were of analytical grade purchased from Merck or S.D. fine chemicals and were used as-received. 2-Vinyl-6-methoxynaphthalene was prepared by the Heck arylation of ethylene with 2-bromo-6-methoxynaphthalene using the NC palladacycle catalyst [12]. The complexes $\text{Pd}(\text{pyca})(\text{PPh}_3)(\text{OTs})\cdot\text{H}_2\text{O}$ was prepared according to the procedure in the literature [5]. The complexes $\text{Pd}(\text{acpy})(\text{PPh}_3)(\text{OTs})_2\cdot 2\text{H}_2\text{O}$, $\text{Pd}(\text{pycald})(\text{PPh}_3)(\text{OTs})_2\cdot 2\text{H}_2\text{O}$, and $\text{Pd}(\text{bipy})(\text{PPh}_3)(\text{OTs})_2\cdot 3\text{H}_2\text{O}$ were prepared as per the procedures described earlier [13].

2.2. Carbonylation reactions and analysis

Carbonylation¹ reactions were carried out in a 50 ml Parr autoclave reactor made of Hastelloy C-276 material, following a procedure similar to that described previously [5]. In a typical reaction, the palladium catalyst and the liquid phase reactants and solvent were charged to the reactor and the reactor was sealed. The contents were heated to the desired temperature, and then the reactor was filled with CO to the desired pressure. Reaction was started by setting agitation speed to 1000 rpm. The progress of the reaction was followed up by observing the pressure drop in CO reservoir as a function of time as well as by taking the intermittent samples of reaction mixture. The reaction was stopped at completion of CO absorption. Afterwards, the reactor was brought to ambient temperature, and pressure was released. The reactor was flushed thrice with N_2 and liquid phase samples were analyzed for reactant/products composition using HP GC 6890 fitted with a HP-1 capillary column (30 m \times 0.33 mm \times 0.2 μm). Products were identified by comparison with authentic materials (calibration data obtained from authentic samples of VMN, product esters and ether at four different concentrations). GC-MS analyses of the samples were performed using Agilent 5973 N Mass Selective Detector attachment.

Molecular weight of the polymer (obtained as a by-product and separated from the reaction mixture) was determined by GPC analysis with chloroform as an eluent having six Ultra Styragel columns (50–10⁵ Å porosities) and UV-100 and RI-150 detectors. Molecular weight (M_n) and polydispersities (M_w/M_n) were determined using a calibration curve obtained by polystyrene standards from PSS Germany. NMR was obtained from Bruker-DRX-500 and Bruker-AV-200. FT-IR spectra were recorded on a PerkinElmer FT-IR spectrum GX instrument by making KBr pellets.

3. Results and discussion

3.1. Preliminary experiments for the hydroesterification of VMN

The palladium complexes containing chelating nitrogen ligands were examined for the first time for the hydroesterification of 2-vinyl-6-methoxynaphthalene to obtain ester of naproxen. Hydroesterification of VMN with methanol was carried out using $\text{Pd}(\text{pyca})(\text{PPh}_3)(\text{OTs})$ as catalyst precursor, *p*-toluenesulfonic acid and LiCl as promoters using methyl ethyl ketone as the solvent. The GC-MS analysis showed the formation of methyl ester of naproxen (methyl 2-(6-methoxy-2-naphthyl)propanoate) and its linear isomer, methyl 3-(6-methoxy-2-naphthyl)propanoate and by-product ether ([2-methoxy-6-(1-methoxyethyl)naphthalene] the product of a simple etherification reaction between the starting olefin and alcohol). But the concentration-time profile for the hydroesterification reaction shown in Fig. 1, does not show equivalent amount of products formed as compared to the reactant consumed. Material balance of the reaction was found to be $\sim 75\%$. This deviation from material balance clearly indicates formation of other components in the reaction mixture that could not be identified by GC analysis. It may be noted that previous literature results do not show any concentration-time profile or quantitative details for this reaction.

To account for this mass balance deviation; the reaction mixture was taken and the solvent was removed. The residue obtained was washed thoroughly with methanol (the Pd-complex, promoters, ester product and ether are soluble in methanol). The residue was further given soxhlet treatment in methanol for 8 h and dried under vacuum. The resulting material was analyzed by ¹H NMR, ¹³C NMR, IR and GPC. These characterizations indicated the formation of a polymer as discussed below.

Molecular weight of the produced polymers was determined by gel permeation chromatography using chloroform as a solvent at room temperature. The GPC analysis showed a single peak and the weight average molecular weight was found to be 29,027. The polymerization can occur because of the high reactivity of the starting material under the reaction conditions. The NMR spectrum of the polymer is shown in Fig. 2. Comparing the NMR spectrum of pure VMN and poly(VMN) indicates that olefin protons corresponding to VMN have disappeared forming broad signals at $\delta = 6\text{--}8$ ppm and at $\delta = 1\text{--}2$ ppm.

The evidence for linear structure was given by the comparison of integration ratio of methoxy group and aromatic group in ¹H NMR

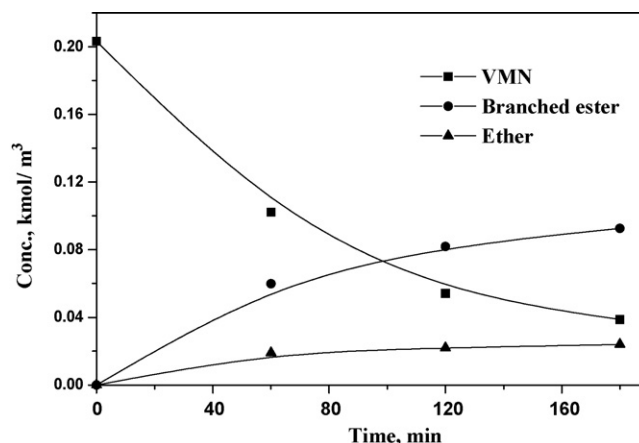


Fig. 1. Concentration vs. reaction time for hydroesterification of VMN. Reaction conditions: VMN, 4.89 mmol; Pd-complex, 0.035 mmol; TsOH, 0.35 mmol; LiCl, 0.35 mmol; P_{CO} , 600 psi; T , 75 °C; MeOH, 2 ml; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol.

¹ Hazardous CO involved, authors suggest safe and expert handling during experiments.

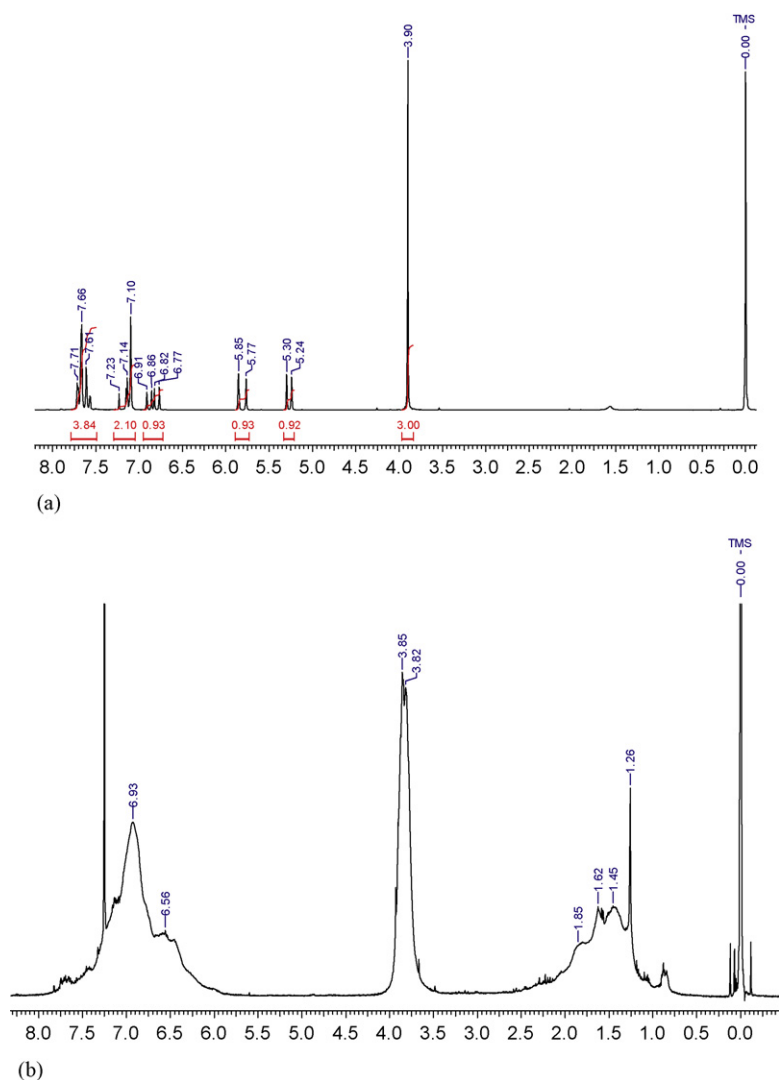


Fig. 2. NMR spectrum of VMN and poly(VMN). (a) ^1H NMR of 2-vinyl-6-methoxynaphthalene. (b) ^1H NMR (500 MHz) spectrum of poly(VMN) ($M_n = 12,360$, $M_w/M_n = 2.347$).

(Fig. 3). The integral ratio is 1:2, which indicates that the obtained poly (VMN) is linear without any cross-linking.

The ^{13}C NMR (Fig. 4) shows the peak values at δ (ppm)=29.67 ($-\text{CH}_2-$), 40.34 ($-\text{CH}$), 55.13 ($-\text{OCH}_3$), 105.59, 118.20, 126.40, 128.76, 132.85, 140.04, 156.93, and the ^{13}C -DEPT shows disappearance of peaks at δ (ppm)=132.85, 140.04, 156.93. ^{13}C -DEPT shows peak

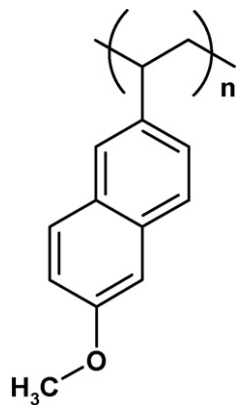


Fig. 3. Structure of poly-VMN.

at $\delta = 29.67$ which corresponds to methylene ($-\text{CH}_2-$) unit, this together with ^1H NMR spectrum indicates the formation of polymer (Fig. 3).

The IR (KBr) spectra shows absorption frequencies at 3438, 2926, 2839, 1635, 1604, 1506, 1482, 1391, 1264, 1159, 1031, 849, 806 and 751 cm^{-1} . The IR spectra revealed the absence of $\text{C}=\text{O}$ stretching vibrations, the peaks arising at 1635, 1604, 1506 cm^{-1} are due to the $\text{C}=\text{C}$ ring stretch. The aromatic $\text{C}-\text{H}$ stretch shows peak at 3438 cm^{-1} and the methyl $\text{C}-\text{H}$ stretch appears at 2926, 2839 cm^{-1} . The absorptions at 1264 and 1031 cm^{-1} can be assigned as benzene ring $\text{C}-\text{O}$ stretch and the methyl $\text{C}-\text{O}$ stretch, respectively.

The ^{13}C NMR and IR results do not show any resonance peaks arising due to $\text{C}=\text{O}$ functionality indicating that the polymer product is not formed in carbonylation reaction sequence but by direct polymerization of the reactant, VMN.

Thus, four different products were identified in the hydroesterification of VMN as shown in Scheme 1. It was observed that the formation of the polymer persists and could not be eliminated by using *tert*-butylcatechol as the polymerization inhibitor. Thus, there is loss of selectivity because of the polymerization of the reactant VMN under reaction conditions. After confirmation and detailed characterization of the polymer as a product, further results obtained in the work are presented based on GC analysis.

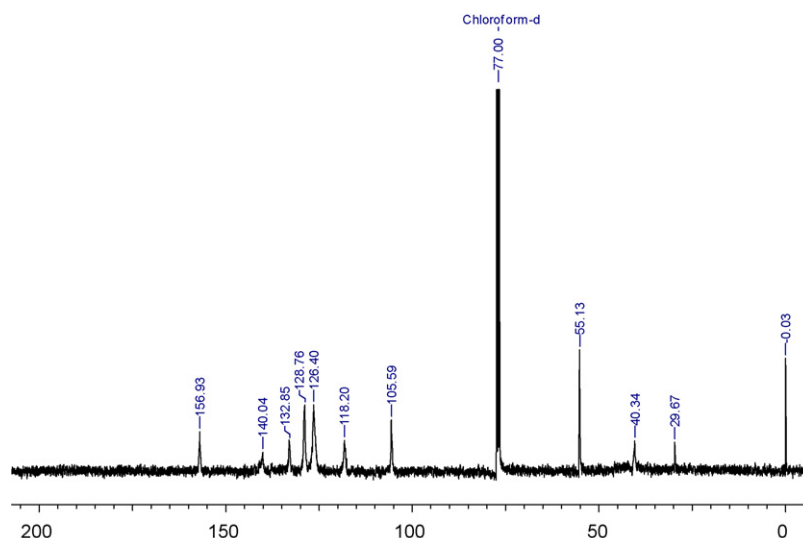
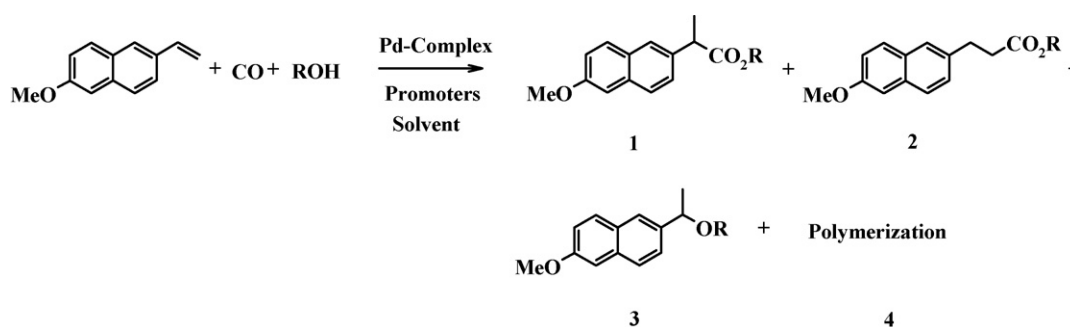


Fig. 4. ^{13}C NMR (500 MHz) spectrum of poly(VMN).



Scheme 1. Hydroesterification of 2-vinyl-6-methoxynaphthalene.

The unaccounted material balance is assigned as the polymerized product.

From the preliminary experiments formation of polymer and ether as the side products was observed under the reaction condition investigated. It is important to understand if palladium has a role in the formation of these unwanted side products. For this purpose few experiments were carried out and the results are presented in Table 1. Under standard reaction conditions (Table 1, entry 1) 84% conversion of VMN with 63.5% selectivity to branched ester, 10.8% selectivity to ether and 25% polymer formation was observed. However, in the absence of palladium complex keeping other conditions constant (Table 1, entry 2) polymer formation was completely suppressed. In this reaction 20% conversion of VMN with ether formation (100% selectivity) was observed. Also, in the reactions carried out at atmospheric N_2 pressure (Table 1, entries 3 and 4) polymer formation was not observed while ether formation (5%

conversion with 100% selectivity) was observed in both the reactions. From the results it can be clearly seen that polymer formation is observed under carbonylation conditions (Pd and CO pressure). In the absence of CO pressure and in the presence of palladium (Table 1, entry 3) polymer formation was not observed. Thus palladium complex formed under carbonylation conditions is active for polymer formation, and also, probably palladium has no role in ether formation.

3.2. Screening of palladium catalysts

Various Pd-complexes were screened for their catalytic activity in hydroesterification of VMN and the results are presented in Table 2. The results show that all the reactions performed are accompanied by the formation of a polymer as well as ether (2-methoxy-6-(1-methoxyethyl)naphthalene). Best result (84% conversion of VMN and 63.5% selectivity to 1) was obtained using $\text{Pd}(\text{acpy})(\text{PPh}_3)(\text{OTs})_2$ as a catalyst precursor (Table 2, entry 3). Further work was carried out using $\text{Pd}(\text{acpy})(\text{PPh}_3)(\text{OTs})_2$ as the catalyst precursor and results are presented below.

3.3. Screening of acid and halide promoters

From the literature it was observed that acid and halide promoters are essential for high activity and selectivity to the branched isomer in the carbonylation of styrene [5,6]. The results are presented in Table 3. In the presence of only acid (*p*-toluenesulfonic acid) promoter, ether (**3**) was formed as the major product (41.7%), the conversion was poor (19%) and the selectivity towards the

Table 1
Preliminary investigations for the formation of side products in the hydroesterification of VMN.

Entry	Conversion (%)	Pd	CO	Selectivity (%)			
				1	2	3	4
1	84	Yes	Yes	63.5	0.6	10.8	25
2	20	No	Yes	–	–	100	–
3	5	Yes	No	–	–	100	–
4	5	No	No	–	–	100	–

Reaction conditions: VMN, 4.89 mmol; $\text{Pd}(\text{acpy})(\text{PPh}_3)(\text{OTs})_2$, 0.035 mmol; TsOH, 0.35 mmol; LiCl, 0.35 mmol; P_{CO} , 600 psi.; T , 75 °C; MeOH, 2 ml; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol; time, 3 h.

Table 2
Results of hydroesterification with different catalyst systems.

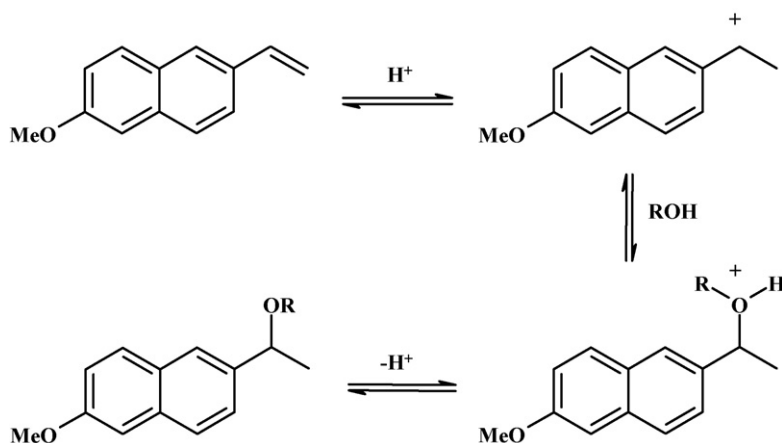
Entry	Catalyst precursor	Conversion (%)	Time (h)	Selectivity (%)				TOF (h ⁻¹)
				1	2	3	4	
1	Pd(pyca)(PPh ₃)(OTs)	74	3	63	0.51	10.8	25	21
2	Pd(pycald)(PPh ₃)(OTs) ₂	69	3	54.4	0.25	15.2	30	17
3	Pd(acpy)(PPh ₃)(OTs) ₂	84	3	63.5	0.6	10.8	25	24
4	Pd(bpy)(PPh ₃)(OTs) ₂	63	3	53.6	0.51	18.7	27	15

Reaction conditions: VMN, 4.89 mmol; Pd-complex, 0.035 mmol; TsOH, 0.35 mmol; LiCl, 0.35 mmol; P_{CO}, 600 psi; T, 75 °C; MeOH, 2 ml; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol.

Table 3
Results of effect of promoter on the hydroesterification reaction.

Entry	Promoter	Conversion (%)	Time (h)	Selectivity (%)				TOF (h ⁻¹)
				1	2	3	4	
1	TsOH	19	3	31.4	6.7	41.7	20	2
2	LiCl	17	3	90.4	–	9.5	–	7
3	TsOH + LiCl	84	3	63.5	0.6	10.8	25	24

Reaction conditions: VMN, 4.89 mmol; Pd-complex, 0.035 mmol; TsOH, 0.35 mmol; LiCl, 0.35 mmol; P_{CO}, 600 psi; T, 75 °C; MeOH, 2 ml; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol.

**Scheme 2.** The formation of ether by the acid-catalyzed reaction of VMN and alcohols.

branched ester was 31.4%. The acid catalyzed formation of the ether can be explained as shown in **Scheme 2**. While using only the halide promoter there is exclusive formation of the branched ester with 90.4% selectivity, polymer was not observed but some ether was formed (9.5%) and the conversion was lower (17%). The simultaneous presence of both acid and halide promoters showed high conversion (84%) with the selectivity of 63.5% towards the branched ester.

3.3.1. Effect of different acid promoters

Since the hydroesterification reaction requires the combination of both the acid and halide promoters, it is necessary to

probe the effect of different promoters for their activity and selectivity. For this purpose, various acid promoters were screened keeping the halide promoter LiCl constant. The results of different acidic promoters on the hydroesterification are presented in **Table 4**. Though the conversion with benzenesulfonic acid as a promoter (96% conversion) was significantly higher, there is not much difference in the selectivity with different promoters. Other sulfonic acids viz. methanesulfonic acid, trifloromethanesulfonic acid also gave good conversions (80–88% conversion). Since high conversion was obtained using benzenesulfonic acid as a promoter, further work was carried using benzenesulfonic acid as the promoter.

Table 4
Results of effect of acid promoter on the hydroesterification reaction.

Entry	Promoter	Conversion (%)	Time (h)	Selectivity (%)				TOF (h ⁻¹)
				1	2	3	4	
1	<i>p</i> -Toluenesulfonic acid	84	3	63.5	0.6	10.8	25	24
2	Methanesulfonic acid	88	3	57.3	0.52	7	35	23
3	Benzenesulfonic acid	96	3	63	0.5	5.9	30	28
4	Trifloromethanesulfonic acid	80	3	54.7	0.71	9.5	35	20
5	Trifluoroacetic acid	72	3	68.6	1.4	1.7	28	23

Reaction conditions: VMN, 4.89 mmol; Pd-complex, 0.035 mmol; acid promoter, 0.35 mmol; LiCl, 0.35 mmol; P_{CO}, 600 psi; T, 75 °C; MeOH, 2 ml; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol.

Table 5

Results of effect of halide promoter on the hydroesterification reaction.

Entry	Promoter	Conversion (%)	Time (h)	Selectivity (%)				TOF (h ⁻¹)
				1	2	3	4	
1	LiCl	96	3	63	0.5	5.9	30	28
2	Bu ₄ NBr	58	3	45.7	2.9	24.3	27	12
3	Bu ₄ NI	29	3	19.6	5.6	54.7	20	2
4	NaCl	72	3	68.8	2.25	3.7	25	23

Reaction conditions: VMN, 4.89 mmol; Pd-complex, 0.035 mmol; benzene sulfonic acid, 0.35 mmol; halide promoter, 0.35 mmol; P_{CO} , 600 psi; T , 75 °C; MeOH, 2 ml; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol.

Table 6

Effect of promoters in the hydroesterification of 2-vinyl-6-methoxynaphthalene.

Entry	H ⁺ :Cl ⁻ ratio	Conversion (%)	Time (h)	Selectivity (%)				TOF (h ⁻¹)
				1	2	3	4	
1	0.175:0.35	89	3	59.5	1	4.3	35	24
2	0.7:0.35	95	3	71.7	0.9	2.1	25	31
3	0.35:0.35	96	3	63	0.5	5.9	30	28
4	0.35:0.7	96	2	63	0.9	5.9	30	42
5	0.35:0.175	82	3	68.4	2.9	3.6	25	26

Reaction conditions: VMN, 4.89 mmol; Pd-complex, 0.035 mmol; P_{CO} , 600 psi; T , 75 °C; MeOH, 2 ml; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol. H⁺ = benzenesulfonic acid, Cl⁻ = LiCl.

3.3.2. Effect of different halide promoters

Having found benzenesulfonic as the promoter of choice, different halide promoters were screened and the results are presented in Table 5. The use of NaCl was also found to be suitable for this reaction though the reaction was slower compared to LiCl. Quaternary ammonium salts such as Bu₄NBr and Bu₄NI favored significant formation of the ether (**3**) (24–55%) and gave poor conversions. Quaternary ammonium salts are phase transfer catalysts and their applications in the etherification reactions have been demonstrated for other substrates [14] previously. Excellent conversions of 96% and selectivity of 63% were observed using LiCl as the promoter. Further work was carried out using LiCl as the promoter.

3.3.3. Effect of benzenesulfonic acid:LiCl ratio

The perfect combination of benzenesulfonic acid and lithium chloride is of considerable importance to tune the reaction to the desired product (excess of the acid promoter can lead to the undesired side reactions such as formation of ether and polymerization). Effect of benzenesulfonic acid:LiCl ratio on hydroesterification of VMN was investigated and the results are presented in Table 6. It was found that with excess of acid promoter (Table 6, entry 2) the ether formation was marginally reduced (<3%); and observed results can be explained as shown in Scheme 2 (the last step to form ether by the removal of proton from the oxonium ion is not favorable in presence of excess acid promoter). Thus, increase in the selectivity towards the branched ester was observed. The conversion of 95% was obtained in 3 h. With excess of lithium chloride (Table 6, entry 4) the conversion of 96% could be achieved in a shorter time of 2 h. There was no large difference in the selectivity pattern for the reaction. Thus best results (96% conversion of VMN with 63%

selectivity to branched ester) were obtained using benzenesulfonic acid:LiCl ratio of 0.35:0.7 and further work was carried out using this ratio.

3.4. Effect of different alcohols

Various alcohols were screened to investigate the hydroesterification reaction and the results are presented in Table 7. Methanol was found to be the alcohol of choice for hydroesterification because of its high polarity and low bulkiness. With increase in the carbon length of the alcohol (decreasing the polarity of alcohol), the selectivity towards the branched ester decreased and ether formation increased. With styrene as substrate ether formation was not reported in the previous literature [15]. The substantial ether formation observed with 2-vinyl-6-methoxynaphthalene as a substrate could be explained by the resonance effect of the electron-donating methoxy group that stabilizes carbocation intermediate (Scheme 2). The carbocation then reacts with the alcohol giving ether [16]. Use of sterically hindered *t*-butylalcohol gave lower conversion of 16%. On increasing the carbon length of alcohol from methanol to *n*-propanol the selectivity of 1 decreased from 63% to 55%, whereas the selectivity to ether increased from 5.9% to 12.6%.

3.5. Effect of different solvents

The hydroesterification was investigated using a variety of organic solvents and the results are outlined in Table 8. The reaction is faster in solvents like toluene and methyl ethyl ketone, while reaction did not proceed using *N,N*-dimethylformamide as a solvent.

Table 7

Effect of alcohols in the hydroesterification of 2-vinyl-6-methoxynaphthalene.

Entry	Alcohol	Conversion (%)	Time (h)	Selectivity (%)				TOF (h ⁻¹)
				1	2	3	4	
1	Methanol	96	2	63	0.9	5.9	30	42
2	Ethanol	96	2	60.2	2.8	6.9	30	40
3	<i>n</i> -Propanol	91	2	55	2.1	12.6	30	34
4	<i>n</i> -Butanol	97	2	47.6	1.1	21	30	32
5	<i>t</i> -Butylalcohol	16	2					

Reaction conditions: VMN, 4.89 mmol; Pd-complex, 0.035 mmol; Benzene sulfonic acid, 0.35 mmol; LiCl, 0.7 mmol; P_{CO} , 600 psi; T , 75 °C; alcohol, 2 ml; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol.

Table 8
Effect of solvents in the hydroesterification of 2-vinyl-6-methoxynaphthalene.

Entry	Solvent	Conversion (%)	Time (h)	Selectivity (%)				TOF (h ⁻¹)
				1	2	3	4	
1	Toluene	98	2	62.9	1	20.2	15	43.9
2	Methyl ethyl ketone	96	2	63	0.9	5.9	30	42
3	Acetone	84	2	58.2	1.3	5.2	35	40.6
4	Methanol	65	2	10.4	10.4	54	25	7.2
5	N,N-dimethylformamide	No reaction	2	–	–	–	–	–

Reaction conditions: VMN, 4.89 mmol; Pd-complex, 0.035 mmol; benzene sulfonic acid, 0.35 mmol; LiCl, 0.7 mmol; P_{CO} , 600 psi; T , 75 °C; MeOH, 2 ml; solvent, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol.

Table 9
Effect of temperature in the hydroesterification of 2-vinyl-6-methoxynaphthalene.

Entry	Temperature (°C)	Conversion (%)	Time (h)	Selectivity (%)				TOF h ⁻¹
				1	2	3	4	
1	55	50	3	88	–	12	–	20
2	65	90	2	67.8	0.75	7.1	25	42
3	75	96	2	63	0.9	5.9	30	42
4	85	98	2	62.1	1	6.6	30	42
5	95	70	2	58.4	2.2	14.1	25	28

Reaction conditions: VMN, 4.89 mmol; Pd-complex, 0.035 mmol; benzene sulfonic acid, 0.35 mmol; LiCl, 0.7 mmol; P_{CO} , 600 psi; MeOH, 2 ml; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol.

Toluene as a solvent gave substantial amounts of ether (20.2%) and marginally lower polymer formation. The differences in selectivity upon changing the solvent are difficult to rationalize at this point. Using methanol as the solvent the activity was lower (65% conversion) with significant amount (54% selectivity) of ether formation and 10% selectivity to branched and linear ester each. The substrate VMN was found to be insoluble in methanol as well as acetone at room temperature. Best results were obtained using methyl ethyl ketone as the solvent.

3.6. Effect of temperature

The hydroesterification was studied in the temperature range of 55–95 °C (Table 9). At 55 °C there was exclusive formation of the branched ester (88% vs. 60–65% at other temperatures) and without forming any polymer, but the conversion was 50%. For the temperature range 65–85 °C, the conversion increased but there was no significant difference in the selectivity pattern for the products obtained. However, further increase in the temperature above 85 °C, caused the decrease in activity, indicating the lower stability of the catalytically active species at higher temperatures. We chose the temperature of 65 °C and further studies were carried out at this temperature.

3.7. Effect of amount of methanol

With methanol as a solvent (Table 8), substantial formation of ether was observed, therefore the effect of methanol concentration was investigated for the hydroesterification reaction and the

Table 10
Effect of amount of methanol at 65 °C.

Entry	Methanol (ml)	Conversion (%)	Time (h)	Selectivity (%)				TOF (h ⁻¹)
				1	2	3	4	
1	2	98	2	67.8	0.75	7.1	25	30
2	1	95	3	71.8	0.3	2.7	25	31
3	0.8	95	3.5	72	0.75	2.2	25	27
4	0.5	80	3.5	78	0.72	1.0	20	25
5	0.25	70	3.5	87.56	–	0.44	12	24

Reaction conditions: VMN, 4.89 mmol; Pd-complex, 0.035 mmol; benzene sulfonic acid, 0.35 mmol; LiCl, 0.7 mmol; P_{CO} , 600 psi; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol.

results are presented in Table 10. It can be seen that with decrease in the concentration of the methanol, the formation of ether was reduced (7.1–0.44%) with increase in the selectivity of the branched ester (67.8–87.5%). As the amount of methanol was reduced from 2 to 0.25 ml it was found that the activity of carbonylation reaction decreases, 98% conversion of VMN was achieved in 2 h using 2 ml of methanol while only 70% conversion was achieved using 0.25 ml of methanol in 3.5 h (Table 10).

3.8. Effect of catalyst loading and carbon monoxide pressure

Effect of catalyst loading and carbon monoxide pressure was studied at a temperature of 65 °C and 0.5 ml of methanol (Table 11). The selectivity towards the linear ester and ether was low under these reaction conditions. When the catalyst loading was doubled keeping the reaction conditions constant, the conversion increased however the polymerization could not be reduced. Similarly with increase in CO partial pressure from 600 to 1000 psi polymer formation was not reduced and 95% conversion of VMN with 68% selectivity to branched ester was obtained in 1 h. Under similar reaction charge but at lower temperature 55 °C (Table 11, entry 6) 99% conversion was achieved in 4.3 h and formation of polymer still takes place. Comparison of this result with that of previous result in Table 9 (entry 1), shows polymer is formed at higher catalyst loading and CO pressures. This again indicates that palladium has a role in the polymerization reaction.

All the reactions have been performed by charging the reactor with the requisite amount of reagents and the gas was filled after the temperature was attained, in this process the reactant VMN

Table 11
Effect of catalyst loading and pressure on the hydroesterification.

Entry	Catalyst (mmol)	Pressure (psi)	Conversion (%)	Time (h)	Selectivity				TOF (h ⁻¹)
					1	2	3	4	
1	0.035	600	80	3.5	78	0.7	1	20	25
2	0.07	600	92	2.5	62	1	2	35	17.3
3	0.07	800	92	2	67	1	2	30	23.4
4	0.07	1000	95	1	68	1	1	30	47.5
5	0.07 ^a	600	94	3.5	67	1	2	30	13.37
6	0.07 ^b	1000	99	4.3	70	0.5	0.5	29	11.3

Reaction conditions: VMN, 4.89 mmol; benzenesulfonic acid, 0.35 mmol; LiCl, 0.7 mmol; MeOH, 0.5 ml; methyl ethyl ketone, 23 ml; 4-*tert*-butylcatechol, 0.03 mmol.

^a CO was filled at room temperature and reaction started.

^b The reaction was carried at 55 °C.

which is having an electron-donating methoxy group is exposed under the reaction conditions of benzenesulfonic acid and lithium chloride till the reaction temperature is attained. There are chances that proton can serve as the initiator for the polymerization. So, in one experiment we filled the CO gas at room temperature and the reactor was heated to the desired temperature. The reaction was monitored by withdrawing samples at regular intervals of time and analyzing by gas chromatography immediately. The results showed 94% conversion of VMN and the selectivity of the desired branched ester was 67%. Thus under our reaction conditions the formation of polymerization could not be completely rooted out.

4. Conclusions

Hydroesterification of VMN has been investigated using palladium complexes containing different nitrogen ligands. Presence of acid and halide promoters was necessary for high catalytic activity and good selectivity to branched ester. Best results were obtained using benzenesulfonic acid and LiCl as promoters. Effect of various reaction conditions on the activity and selectivity was investigated and it was observed that ether and polymer formed as by-products under all reaction conditions. Ether formation was suppressed with decrease in methanol concentration. Polymer formed was characterized by GPC and NMR analysis; experiments revealed polymer formation was catalyzed by palladium under reaction conditions. Various alcohols were screened and with *t*-butanol product formation was not observed. Selectivity to branched ester was found to decrease with increase in chain length of the carbon for alcohols screened. Temperature was found to have significant effect on the reaction and polymer formation was not observed at 55 °C with 88% selectivity to iso ester. Selectivity to iso ester decreased with increase in temperature of the reaction. This is the first report on

the use of palladium complexes containing nitrogen ligands for hydroesterification of VMN.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.03.021.

References

- [1] G. Kiss, Chem. Rev. 101 (2001) 3435–3456.
- [2] F. Piacenti, M. Bianchi, R. Lazzaroni, Chim. Ind. (Milan) 50 (1968) 352.
- [3] J. Tsuji, Acc. Chem. Res. 2 (1969) 96.
- [4] Y. Sugi, K. Bando, Chem. Lett. 5 (1976) 727; J.F. Knifton, J. Org. Chem. 41 (1976) 2885; R. Naigre, T. Chenal, I. Cipres, P. Kalck, J.C. Daran, J. Vaissermann, J. Organomet. Chem. 480 (1994) 91.
- [5] S. Jayasree, A. Seayad, R.V. Chaudhari, Org. Lett. 2 (2000) 203–206.
- [6] A. Seayad, S. Jayasree, R.V. Chaudhari, J. Mol. Catal. A 172 (2001) 151–164.
- [7] A. Seayad, S. Jayasree, R.V. Chaudhari, Org. Lett. 1 (1999) 459–461.
- [8] H. Tamejiro, W. Noriko, K. Tetsuo, Synlett 8 (1991) 569–570.
- [9] J. Zhang, C.-G. Xia, J. Mol. Catal. A 206 (2003) 59–65.
- [10] Y. Kawashima, K. Okano, K. Nozaki, T. Hiyama, Bull. Chem. Soc. Jpn. 77 (2004) 347–355.
- [11] S. Oi, M. Nomura, T. Aiko, Y. Inoue, J. Mol. Catal. A 115 (1997) 289–295.
- [12] S.B. Atla, A.A. Kelkar, V.G. Puranik, W. Bensch, R.V. Chaudhari, J. Organomet. Chem. 694 (2009) 683–690.
- [13] J. Seayad, Thesis submitted to Pune University, 2000.
- [14] Stapp, Paul R, US Patent 4,299,998 (1981).
- [15] A. Seayad, A.A. Kelkar, L. Toniolo, R.V. Chaudhari, J. Mol. Catal. A 151 (2000) 47–59.
- [16] J.M. Adams, D.E. Clement, S.H. Graham, Clays Clay Miner. 31 (1983) 129.