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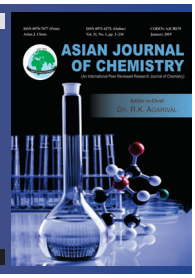

Highly Efficient Rhodium-Phosphite Catalyzed Hydroformylation of Camphene and other Terpenes

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The hydroformylation of terpenes has been studied with homogeneous Rh, Co and Pt complexes. The rhodium complex, $Rh(CO)_2(acac)$ modified with triphenyl phosphite ligand has been found to be the best catalyst system for hydroformylation of camphene and other terpenes. The role of ligands, solvents, Rh:P ratio and reaction conditions on the activity and selectivity towards camphene hydroformylation have been investigated.

Keywords: Homogeneous, Hydroformylation, Camphene, Terpenes, Rhodium phosphite.

INTRODUCTION

Terpenes represent a renewable and useful source of inexpensive olefins derived from citrus and pine oils. They are a natural and sustainable supply of building blocks for the fine chemical industry. Hydroformylation of these naturally occurring olefinic monoterpenes seems to be a promising synthetic route to obtain a wide variety of aldehydes with applications in the perfume, flavour and pharmaceutical industries [1-6]. Optically pure terpenes containing prochiral centers are easily available and their stereoselective functionalization could be useful for the production of chiral synthetic intermediates (chiral synthones) [2]. One of the major problems in hydroformylation of these terpenes is the prolonged reaction time and severe reaction conditions (>100 ºC, > 5 MPa syngas pressure) resulting in the lower TOF of the catalysts [3-6] as compared to other olefins. Thus, the low reactivity of terpenes, their isomerization tendency and poor regio- and stereoselectivity towards hydroformylation products are the major challenges in hydroformylation of terpenes.

Hydroformylation of monocyclic and bicyclic monoterpenes and terpenoids such as camphene [7-14] limonene [9, 15-26], β-pinene [9,13,27-30] and carvone [20,31,32] has been reported using homogeneous cobalt and rhodium complex catalysts. Alternatively platinum-tin catalytic systems have also been investigated for the hydroformylation of camphene [12, 33,34], (+)-R-limonene [9,18,20,33], β-pinene [33] and carvone [20]. Rhodium complexes modified with phosphorus ligands usually promote the preferable formation of *cis*-10-formyl pinane or corresponding acetal and allow a higher chemoselectivity in hydroformylation of β-pinene [27]. On the other hand, it has been reported that presence of phosphite ligands favours the formation of *trans*-aldehyde, but they are not efficient in suppressing substrate isomerization [30]. Hydroformylation of camphene gave linear aldehyde (exo and endo) with both modified and unmodified rhodium catalyst systems. The addition of phosphorus ligands favours the formation of endo isomer (exo/endo=1/1.5), whereas the exo/endo ratio is 1/1 in unmodified systems [12]. Hydroformylation of limonene using dinuclear rhodium complexes $[Rh(COD)Cl]_2$ along with various bulky phosphite ligands *e.g.* *tris*(2-*t*-butylphenyl)phosphite, *tris*(2-phenylphenyl)phosphite, *tris*(2-*t*-butyl 4-methyl phenyl)-phosphite gives very high rates (TOF = 1500-4000 h^{-1}) as compared to Rh-TPP system (TOF ≤100) [35,36]. The dinuclear rhodium complexes $[Rh_2(\mu\text{-}SR)_2(CO)_2L_2]$, with L = PPh_3, $P(OPh)_3$ or $P(OMe)_3$ were found to give moderate activities for hydroformylation of limonene, α-, β-pinene, (-)-camphene and other terpenes [9,20]. Hydroformylation of endocyclic double bonds in para-menthenic terpenes such as terpinolene, γ-terpinene and α-terpinene under mild conditions has been investigated by da Silva *et al.* [37]. Aqueous biphasic and ionic liquid toluene

biphasic hydrformylation of some terpenes has been reported recently [38,39].

The diastereomeric excess (d.e.) achieved for exo and endo aldehyde product in the hydroformylation of camphene with both rhodium and platinum complexes bearing either achiral or chiral ligands is relatively low [33,34]. Although hydroformylation of various terpenes with different transition metals complex catalysts has been studied previously, their rates of hydroformylation were generally very poor [13]. The most studied terpenes were limonene and β-pinene. The highest rates were observed for monocyclic terpene such as limonene [18,35] but for bicyclic terpenes like β-pinene and camphene poor rates (TOF < 100 h^{-1}) were observed due to their steric properties.

The use of phosphite ligands for rhodium complex catalyzed hydroformylation of terpenes has also not been investigated in detail. In this work, we have demonstrated hydroformylation of camphene and other terpenes using a highly efficient $Rh(CO)_2$-(acac)/$P(OPh)_3$ catalyst for the first time. The effect of different parameters on activity and selectivity in the hydroformylation of camphene using $Rh(CO)_2(acac)/P(OPh)_3$ catalyst was studied.

EXPERIMENTAL

Rhodium(III) chloride trihydrate ($RhCl_3 \cdot 3H_2O$, 40 % Rh), cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and chloroplatinic acid ($H_2[PtCl_6]$) were obtained from Hindustan Platinum (Mumbai, India) and used as received. (-)-Camphene, R-(+)-limonene, (-)-β-pinene, γ-terpinene, 3-(-)-carene, α-pinene, R-(-) carvone, myrcene, citral, (±)-β-citronellol, $P(OPh)_3$, $P(OBu)_3$, $P(OEt)_3$, *bis*(diphenylphosphino)ethane (dppe), *bis*(diphenylphosphino)-propane (dppp), *bis*(diphenylphosphino)butane (dppb), 1,5-cyclooctadiene and cobalt(II) acetate tetrahydrate, were procured from Sigma-Aldrich, USA and used without further purification. Triphenyl phosphine (PPh_3), acetyl acetone, potassium acetate, KOH, HCHO solution (40 % w/w), $NaBH_4$, dimethylformamide (DMF), acetic acid were purchased from Loba Chemie India. The solvents ethanol, methanol, methyl ethyl ketone, 1,2-dichloroethane (DCE), dichloromethane (DCM), xylene, toluene, hexane, cyclohexane, petroleum ether, ethyl acetate obtained from Merck, India were freshly distilled and dried prior to use. Hydrogen and nitrogen gas supplied by Indian Oxygen, Mumbai and carbon monoxide (> 99.8 % pure, Matheson Gas USA) were used directly from the cylinders. The syngas mixture ($CO + H_2$) 1:1 was prepared by mixing H_2 and CO in a reservoir vessel. The complexes $HRh(CO)(PPh_3)_3$ [40], $Rh(CO)_2(acac)$ [41], $[Rh(COD)Cl)]_2$ and $[Rh(\mu\text{-}OAc)(COD)]_2$ [42], $[Rh(\mu\text{-}OMe)(COD)]_2$ [43], $Co_2(CO)_8$ [44] and *cis*-$PtCl_2(PPh_3)_2$ [45] were prepared using literature procedures.

Experimental setup and procedure: All the hydroformylation experiments were carried out either in a 50 mL autoclave, made of stainless steel, supplied by Amar Instruments India Pvt. Ltd. or a 300 mL Parr reactor (Parr instruments, USA). The reactor setup was similar to that reported earlier [40].

In a typical experiment, known quantities of catalyst, ligand, olefin (terpene), and the solvent were charged into the autoclave and the reactor was flushed with nitrogen. The contents were then flushed with a mixture of CO and H_2 and heated to a desired temperature. A mixture of CO and H_2, in the required ratio (1:1), was introduced into the autoclave, a sample of liquid withdrawn, and the reaction started by switching the stirrer on. The reaction was then continued at a constant pressure by supply of $CO + H_2$ (1:1) from the reservoir vessel. Since, the major products formed were aldehydes, supply of $CO + H_2$ at a ratio of 1:1 (as per stoicheometry) was adequate to maintain a constant composition of CO and H_2 in the autoclave, as introduced in the beginning. This was confirmed in a few cases by analysis of the CO content in the gas phase at the end of the reaction. In each run, samples were withdrawn at regular intervals of time and analysed for reactants and products in order to check the material balance. The reproducibility of the experiments was found to be in a range of 5-7 %.

Analytical methods: The quantitative analysis of reactant and hydroformylation products was carried out by an external standard method using a gas chromatographic technique. For this purpose, HP 6890 gas chromatograph controlled by the HP Chemstation software and equipped with an auto sampler unit, fitted with HP-5 capillary column (30 M × 320 μm × 0.25 μm film thickness with a stationary phase of 5 % diphenyl 95 % dimethyl polysiloxane) and FID detector was used.

The terpenes hydroformylation products were identified on GC-MS (Agilent 6890N with MS 5973N mass selective detector on a similar column.). The formation of the products was confirmed by comparison with the library fragmentation patterns available and with a > 90 % match. The aldehyde products obtained after hydroformylation of camphene, limonene, β-pinene, 3-carene, γ-terpinene and carvone were isolated from the reaction mixture by distillation under reduced pressure. They were separated by column chromatography (silica). The products of terpenes hydroformylation were identified using GC-MS.

***exo*-3,3-Dimethyl-2-norbornaneacetaldehyde (7a) shorter GC retention time):** IR (KBr, ν_{max}, cm^{-1}): 1726, 2713 (CHO), 1366, 1385 (mixed dimethyl). MS (*m/z* rel. int.): 166/4 (M^+); 133/15; 122/53; 109/31; 107/52; 97/100; 83/22; 81/32; 79/41; 69/47; 67/51; 55/40; 41/44.

***endo*-3,3-Dimethyl-2-norbornaneacetaldehyde (7b), longer GC retention time):** IR (KBr, ν_{max}, cm^{-1}): 1726, 2713 (CHO), 1366, 1385 (mixed dimethyl). MS (*m/z* rel. int.): 166/3; (M^+); 133/11; 122/38; 109/22; 107/39; 97/100; 83/18; 81/24; 79/31; 69/37; 67/40; 55/30; 41/35.

3-(4-Methylcyclohex-3-enyl)butanal (11): MS (*m/z* rel. int.): 166/7 (M+); 148/47; 133/33; 121/25; 106/34; 91/59; 93/100; 67/57; 55/23; 41/26.

1-Methyl-4-(propan-2-ylidene)cyclohex-1-ene (12) (isomerized limonene): MS (*m/z* rel. int.): 136/86 (M^+); 121/100; 105/22; 93/85; 91/43; 79/31; 77/25.

***cis*-10-Formylpinane (13a), longer GC retention time):** MS (*m/z* rel. int.): 166/2 (M^+); 151/18; 133/17; 122/90; 107/52; 95/31; 93/30; 81/57; 79/100; 69/69; 67/71; 55/80; 41/82.

***trans*-10-Formylpinane (13b), shorter GC retention time):** MS (*m/z* rel. int.):166/3 (M^+), 151/23; 133/21; 122/91; 107/54; 93/32; 81/62; 79/100; 69/68; 67/68; 55/86; 41/80.

α-Pinene (14) (isomerized product of β-pinene): MS (*m/z* rel. int.): 136/10 (M^+); 121/13; 105/10; 93/100; 77/25; 41/9.

2-Caranecarbaldehyde (15) or (3,7,7-trimethylbicyclo [4.1.0]heptane-2-carbaldehyde): MS (*m/z* rel. int.): 166/6 (M^+);

151/22; 137/94; 123/9; 109/34; 105/27; 95/81; 93/39; 81/100; 69/42; 67/42; 55/43; 41/40.

3-Caranecarbaldehyde (16) or (3,7,7-trimethylbicyclo-[4.1.0]heptane-3-carbaldehyde): MS (*m/z* rel. int.): 166/19 (M^+); 151/31; 135/77; 123/48; 109/33; 105/27; 93/100, 81/94; 67/69; 55/48; 41/63.

3-Isopropyl-6-methylcyclohex-3-enecarbaldehyde (17) (major): MS (*m/z* rel. int.): 166/43 (M^+); 151/17; 137/61; 123/26; 109/24; 93/100; 81/63; 67/26; 55/26; 43/30.

6-Isopropyl-3-methylcyclohex-3-enecarbaldehyde (18) (minor): MS (*m/z* rel. int.): 166/43 (M^+); 151/17; 137/61; 123/26; 109/24; 93/100; 81/63; 67/26; 55/26

1-Isopropyl-4-methylcyclohex-1-ene (19): MS (*m/z* rel. int.): 138/32 (M^+); 123/24; 95/100; 81/69; 6729; 55/14; 41/15.

4-Isopropyl-1-methylcyclohex-1-ene (20) MS (*m/z* rel. int): 138/34 (M^+); 179/34; 95/100; 81/27; 68/40; 67/44; 55/15; 41/16.

3-Isopropyl-6-methylcyclohexa-1,4-diene (21) (isomerized product): MS (*m/z* rel.int): 136/54 (M^+);121/100; 105/17; 93/75; 91/36; 79/21; 77/25.

3-(4-Methylcyclohex-4-en-3-onyl)butanal (22)(major): MS (*m/z* rel.int.): 180/3 (M^+); 162/5: 136/65; 109/100; 82/40.

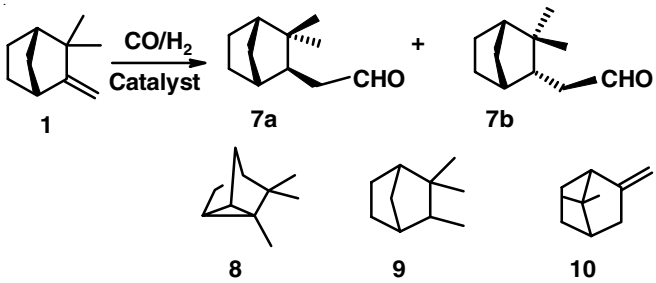
5-(4-Hydroxybutan-2-yl)-2-methylcyclohex-2-enone (23): MS (*m/z* rel. int.): 182/22 (M^+); 138/47; 122/33; 109/100; 94/30; 81/27; 69/39; 55/33; 41/42.

3-(4-Methyl-3-oxocyclohexyl)butanal (24): MS (*m/z* rel. int.): 182/1 (M^+); 164/6; 138/100; 111/67, 95/33, 81/24, 69/35; 55/70; 41/41.

5-Isopropyl-2-methylcyclohex-2-enone (25): MS (*m/z* rel. int.): 152/100 (M^+); 137/32; 109/60; 95/25; 81/65; 69/70; 41/41.

RESULTS AND DISCUSSION

Catalyst screening studies: As a preliminary investigation, hydroformylation of camphene was carried out in toluene at 373 K in the presence of the various Rh, Co and Pt complexes and the results are presented in Table-1. The products found in all cases were the terminal aldehyde. Hydroformylation of camphene (**1**) is found to give only the terminal aldehyde 3,3-dimethyl-2-norbornaneacetaldehyde, as a diastereomeric mixture of exo (**7a**) and endo (**7b**) isomers. A small quantity of byproducts namely tricyclene (**8**) and isocamphane (**9**) are formed by hydrogenation side reaction while fenchene (**10**) was obtained as a byproduct by isomerization reaction (**Scheme-I**).



Scheme-I: Hydroformylation of camphene

The Wilkinson's catalyst showed poor catalytic activity (TOF = 14 h^{-1}) in the hydroformylation of camphene (entry 1, Table-1) and gave linear aldehydes along with hydrogenated and isomerized products (~9 %). On the other hand, the unmodified rhodium complex catalysts such as $Rh(CO)_2(acac)$ and $[Rh(COD)Cl)]_2$ showed improved activity over Wilkinson's catalyst (entry 2, Table-1). When phosphite ligand was added to this catalyst, the activity and selectivity increased dramatically (entry 4, Table-1). The $Rh(CO)_2(acac)/P(OPh)_3$ catalyst system gave the highest catalytic activity (TOF =186 h^{-1}) with 99 % selectivity to linear aldehyde (with d.e. = 9 % to *endo*). The possible reason for the observed rate enhancement could be the facile dissociation of phosphite ligand [18,35,46-48] which facilitates faster coordination of olefins to the metal center. This results in better stabilization of the intermediate catalytic species. Similar observation of rate enhancement was reported for linear as well as internal olefin hydroformylation using Rh-phosphite complex catalysts [46]. The hydrogenation and isomerized camphene products (**8**, **9** and **10**) also reduced substantially with the phosphite containing catalyst. This suggests that the presence of phosphite ligand suppresses the side reactions like isomerization and hydrogenation.

Dimeric rhodium complexes such as $[Rh(COD)Cl)]_2$, $[Rh(\mu\text{-}OMe)(COD)]_2$, $[Rh(\mu\text{-}OAc)(COD)]_2$ in the presence of phosphite ligand showed lower activity compared to the $Rh(CO)_2(acac)/P(OPh)_3$ complex catalyst (entry 5-7; Table-1). The dissociation of the dimer to monomeric species is known to be a slower step [49], and hence results in lower activity. No reaction was observed using complexes of cobalt and platinum under similar reaction conditions (entry 8-11; Table-1). This is probably due to the fact that these catalysts are effective at higher syngas pressure (> 9 MPa) compared to the existing conditions [7,8,33,34].

TABLE-1
SCREENING OF CATALYST FOR HYDROFORMYLATION OF CAMPHENE

Run No.	Catalyst	Time (h)	Conversion (%)	Aldehyde selectivity (%)	iso/hd. camphene (%)	exo/endo	TOF (h^{-1})
1	$HRhCO(PPh_3)_3$	24.9	98.3	91.8	9.2	1.18	14
2	$Rh(CO)_2$ (acac)	18.1	97.6	92.7	7.3	1.24	16
3	$[Rh(COD)Cl)]_2$	16.0	96.7	97.9	2.1	1.22	23
4	$Rh(CO)_2(acac)/P(OPh)_3$	1.8	94.3	98.8	1.2	0.84	186
5	$[Rh(COD)Cl)]_2/P(OPh)_3$	5.0	99.1	98.7	1.3	0.89	57
6[a]	$[Rh(\mu\text{-}OAc)COD]_2)/P(OPh)_3$	4.0	81.6	99.4	0.6	0.64	72
7[a]	$[Rh(\mu\text{-}OMe)COD]_2)/P(OPh)_3$	4.0	96.2	99.5	0.5	0.65	85
8[b]	$Co(acetate)_2$/ PPh_3	8.3	No reaction				
9[b]	$Co_2(CO)_8$	9.1	No reaction				
10[b]	$Co(acetate)_2$/ $P(OPh)_3$	7.0	Catalyst formation was not observed.				
11[b]	$PtCl_2(PPh_3)_2$	7.0	Platinum metal precipitates out.				

Reaction conditions: Camphene: 0.64 kmol/m^3, catalyst: 1.23×10^{-3} kmol/m^3, ligand: 7.4×10^{-3} moles (Rh:P = 1:6), T: 373 K, agitation speed : 16.6 Hz, P_{CO+H2}: 4.14 MPa, solvent: toluene, total charge: 8.1×10^{-5} m^3 a = Solvent: MEK, b = P_{CO+H2} : 8.6 MPa

Effect of solvent: Solvents are known to play a major role in the activity as well as selectivity in hydroformylation reactions. To understand the role of solvents in hydroformylation of camphene, reactions were taken in a number of solvents using $Rh(CO)_2(acac)/P(OPh)_3$ catalyst. It was observed that the solvents have a prominent influence on the selectivity and activity of the catalyst. The rates of hydroformylation were higher in polar protic (ethanol, methanol, methyl ethyl ketone) solvents and lower in non-polar solvents (cyclohexene, hexane). Methanol and ethanol gave higher rates (TOF 486 and 488 h^{-1}, respectively) but acetals (96.6 and 35.7 %, respectively) were formed by condensation of aldehyde with alcohol solvents. The best activity with 100 % selectivity to aldehydes was observed in methyl ethyl ketone wherein a TOF of 417 h^{-1} was observed. In general, solvents with a higher polarity gave better activity over those with a lower polarity in hydroformylation of olefins [50]. A comparison of the relative polarity of solvents with the activity and *exo*/*endo* ratio of the products (Fig. 1) for the hydroformylation of camphene. It was also observed that with decrease in polarity of solvents, the distereoselectivity towards *exo* product increases.

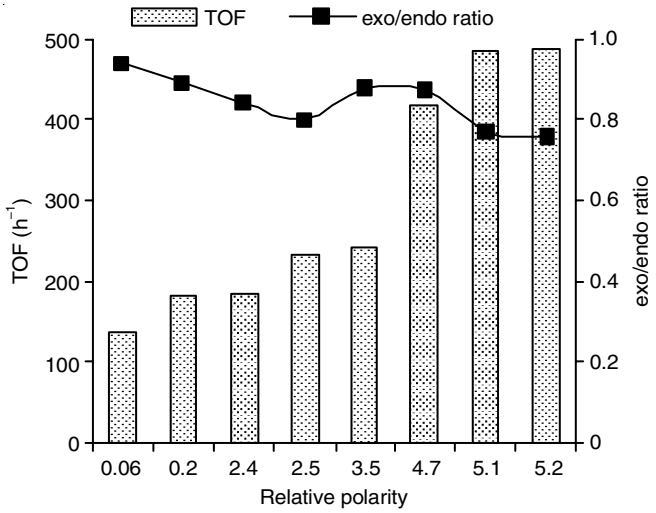


Fig. 1. A plot of activity and exo/endo ratio *vs.* relative polarity; Reaction conditions: camphene: 0.64 kmol/m^3, $Rh(CO)_2(acac)$: 1.23×10^{-3} kmol/m^3, $P(OPh)_3$: 7.4×10^{-3} kmol/m^3 (Rh:P = 1:6), T: 373 K, agitation speed: 16.6 Hz, P_{CO+H_2}: 4.14 MPa, total charge: 8.1×10^{-5} m^3. % (hexane 0.06, cyclohexane 0.2, toluene 2.4, xylene 2.5, 1,2 DCE 3.5, MEK 4.7, methanol 5.1, ethanol 5.2)

Screening of ligands: The type and nature of ligands is known to have a dramatic influence on the activity and selectivity of homogeneous catalytic reactions [51]. The influence of phosphite ligands on the activity and selectivity of the $Rh(CO)_2(acac)$ catalyst was investigated for the hydroformylation of camphene in methyl ethyl ketone solvent at 373K. The results are presented in Table-2. Triphenylphosphite [$P(OPh)_3$], triethylphosphite [$P(OEt)_3$] and tri-(*n*-butyl)phosphite [$P(OBu)_3$] promoted Rh catalyst systems were found to be active for the hydroformylation of camphene. However, Rh/triphenyl phosphite catalyst was by far the most active catalyst for camphene hydroformylation. This observation can be explained on the basis of the electronic factor *i.e.* higher electronegativity (χ) value of $P(OPh)_3$ with respect to $P(OBu)_3$ and $P(OEt)_3$. The high electronegativity of the ligand makes rhodium centre electron deficient, and induces a fast replacement of CO ligand, which promotes faster coordination of olefin to rhodium centre [52]. The high *exo*/*endo* ratio observed is due to the larger cone angle of $P(OPh)_3$ (128º) compared to $P(OEt)_3$, (123º) and $P(OBu)_3$ (109º). No reaction was observed when bidentate ligands such as diphenylphosphinoethane (dppe), diphenylphosphinopropane (dppp) and diphenylphosphinobutane (dppb) were used under similar reaction conditions. These bidentate ligands are known to be less active even for the hydroformylation of linear olefins as compared to the monodentate ligands [53], and hence their activity for a hindered olefin like camphene is expected to be much less.

Effect of P/Rh ratio: The dependence of activity and product distribution on the P/Rh ratio for camphene hydroformylation was studied using $Rh(CO)_2(acac)$ in presence of additional $P(OPh)_3$ ligand. The results are presented in Fig. 2. The effect of Rh to phosphite ratio on activity was studied in the initial range of olefin conversion (~ 35 %). A strong negative effect of $P(OPh)_3$ concentration on activity of camphene hydroformylation was observed. The activity increases with the concentration of ligand upto Rh:P of 1:3. Thereafter, it decreases on further phosphite addition from a Rh:L ratio of 1:3 (TOF = 1029 h-1) to 1:12 (TOF = 273 h^{-1}). The aldehyde selectivity, however, remains unaffected (> 99 %). The highest activity was observed at a P/Rh ratio of three as seen in Fig. 2. At low P/Rh ratio, the phosphite ligand is partially replaced by a carbonyl ligand resulting in a higher rate. As per the hydroformylation mechanism, the phosphite dissociation must occur to form the coordinatively unsaturated intermediate. This dissociation is suppressed by increased $P(OPh)_3$ concentration, which serves to reduce the concentration of active Rh species in the catalytic cycle. This observation of inhibition in rate also supports the hydroformylation mechanism using phosphite ligand [54].

TABLE-2
LIGAND SCREENING STUDIES FOR HYDROFORMYLATION OF CAMPHENE

S. No.	Ligand	Conversion (%)	Aldehyde selectivity (%)	iso./hd. camphene (%)	exo/endo	TOF (h^{-1})	Time (h)
1	$P(OPh)_3$	99.2	99.4	0.6	0.87	419	1.3
2	$P(OEt)_3$	20.7	99.2	0.8	0.71	20	9.0
3	$P(OBu)_3$	74.9	99.5	0.5	0.69	29	9.0
4	dppe	No reaction	No reaction	No reaction	No reaction	No reaction	7.0
5	dppp	No reaction	No reaction	No reaction	No reaction	No reaction	7.0
6	dppb	No reaction	No reaction	No reaction	No reaction	No reaction	7.0

Reaction conditions: $Rh(CO)_2(acac)$: 1×10^{-3} kmol/m^3, ligand: 3×10^{-3} kmol/m^3, camphene: 0.37 kmol/m^3, Rh:P = 1:3, MEK: 2.82×10^{-5} m^3, total charge : 3.0×10^{-5} m^3 , T: 373 K P_{CO+H2}: 4.14 MPa, agitation speed : 16.6 Hz

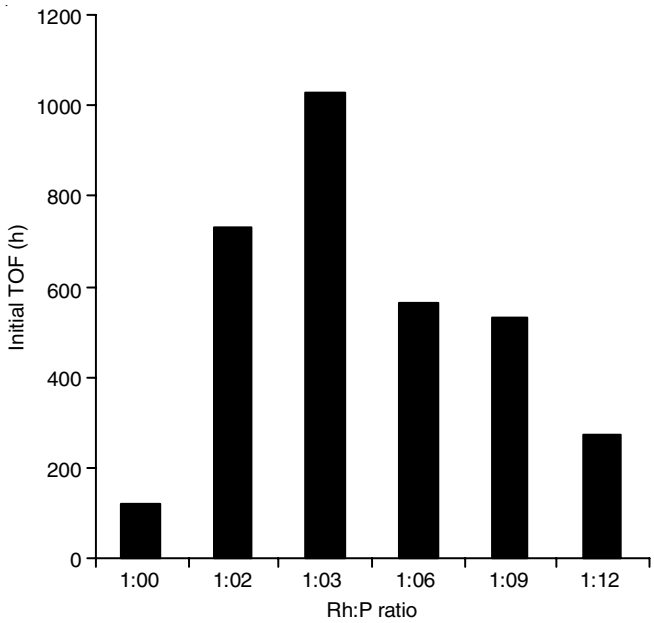
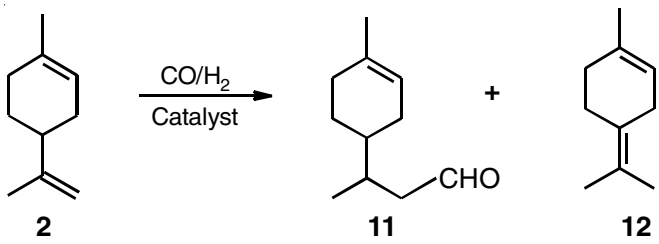
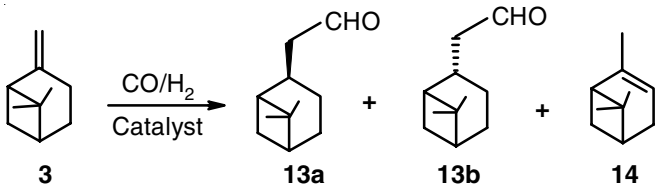


Fig. 2. A plot of initial activity *vs.* Rh:P ratio; Reaction conditions: $Rh(CO)_2(acac)$: 1×10^{-3} kmol/m^3, camphene: 0.37 kmol/m^3, T: 373 K, P_{CO+H_2}: 4.14 MPa, MEK: 2.82×10^{-5} m^3, total charge: 3.0×10^{-5} m^3, agitation speed: 16.6 Hz

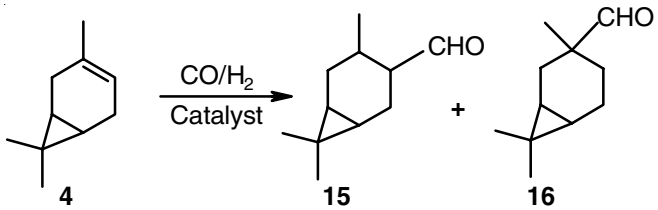
Hydroformylation of various terpenes and terpenoids using $Rh(CO)_2(acac)/P(OPh_3)_3$ catalyst: The highly active $Rh(CO)_2(acac)/P(OPh)_3$ catalyst was tested for the hydroformylation of other terpenes at a total pressure of 4.14 MPa ($CO/H_2 = 1$), $Rh(CO)_2(acac)$: 1×10^{-3} kmol/m^3, $P(OPh)_3$: 3×10^{-3} kmol/m^3, and terpene concentration of 0.37 kmol/m^3 at 373 K. The results are presented in Table-3. In addition to hydroformylation of camphene (**1**), the catalyst was found to be very active for the hydroformylation of R(+)-limonene (**2**) (**Scheme-II**) and α-pinene (**3**) (**Scheme-III**). Less hydroformylation activity was observed for 3-carene (**4**) (**Scheme-IV**) and γ-terpinene (**5**) (**Scheme-V**). The hydroformylation of limonene (**2**) and β-pinene (**3**) gives 3-(4-methylcyclohex-3-enyl)butanal (**11**) and *cis*- (**13a**) and *trans*- (**13b**) 10-formylpinane by hydroformylation and isomerized limonene (**12**) and α-pinene (**14**) as isomerization byproducts, respectively. The hydroformylation of 3-carene (**4**) gives 2-caranecarbaldehyde (**15**) and 3-caranecarbaldehyde (**16**) in equal proportion. For γ-terpinene isomerization and hydrogenation activity was more as compared to hydroformylation activity. γ-Terpinene (**5**) on hydroformyl-



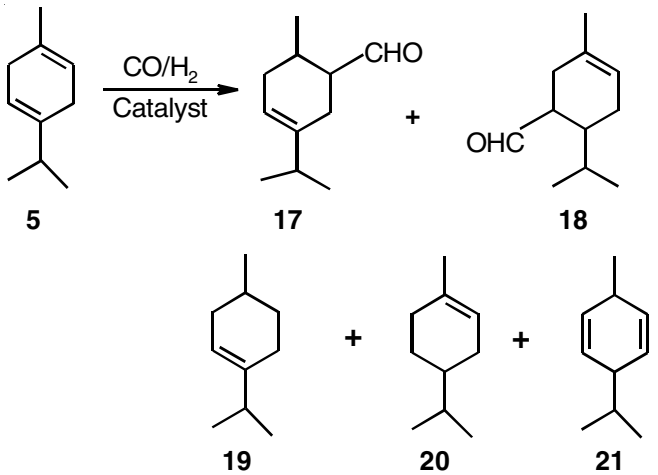
Scheme-II: Hydroformylation of limonene



Scheme-III: Hydroformylation of β-pinene



Scheme-IV: Hydroformylation of 3-carene



Scheme-V: Hydroformylation of γ-terpinene

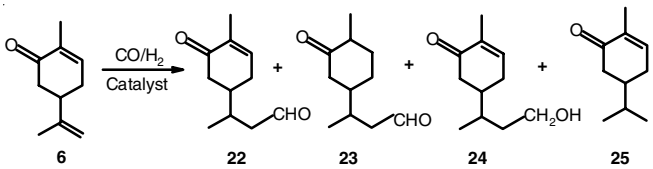
TABLE-3
SCREENING OF TERPENES USING $Rh(CO)_2(acac)/P(OPh)_3$ IN METHYL ETHYL KETONE

Run No.	Terpene	Conversion (%)	Aldehyde selectivity (%)	iso/hd. terpenes (%)	exo/endo or *cis/trans* ratio	TOF (h^{-1})	Time (h)
1	(-)-Camphene	99.2	99.4	0.6	0.87	419	1.3
2	(R)-Limonene	99.3	99.4	0.6	-	526	0.7
3	β-Pinene	78.9	70.0	30.0	0.88	56.6	3.3
4	γ-Terpinene	45.5	28.0	72.0	-	9.2	5.0
5	3-Carene	10.7	98.3	1.7	-	9.5	4.0
6	R-(-) Carvone*	94.4	92.7	1.0	-	688	0.5
7	α-Pinene	No reaction					4.0
8	Myrcene	No reaction, only isomerization is observed					7.3

*Reaction in toluene as substrate is insoluble in MEK, alcohol selectivity of 6.3 %; Reaction conditions: $Rh(CO)_2(acac)$: 1×10^{-3} kmol/m^3, $P(OPh)_3$: 3×10^{-3} kmol/m^3, Rh:P = 1:3, terpene: 0.37 kmol/m^3, T: 373 K, P_{CO+H2}: 4.14 MPa, agitation speed: 16.6 Hz, MEK: 2.82×10^{-5} m^3, total charge: 3.0×10^{-5} m^3

ation gives 3-isopropyl-6-methylcyclohex-3-ene carbaldehyde (**17**) as a major and 6-isopropyl-3-methylcyclohex-3-ene carbaldehyde (**18**) as a minor aldehyde product. The other products formed are hydrogenated products such as (1-isopropyl-4-methylcyclohex-1-ene (**19**) and 4-isopropyl-1-methylcyclohex-1-ene (**20**) and isomerized product (3-isopropyl-6-methylcyclohexa-1,4-diene (**21**) by hydrogenation and isomerization side reaction (**Scheme-V**). No reaction was observed with α-pinene and myrcene. In case of myrcene only isomerization was observed.

The catalyst was found to be more active for hydroformylation of carvone (**6**) (**Scheme-VI**) as compared to camphene and limonene and a TOF of 688 h^{-1} was obtained. The major product for carvone hydroformylation is 3-(4-meth1cyclohex-4-en-3-onyl)butanal (**22**). The other minor products include 3-(4-methyl-3-oxocyclohexyl)butanal (**23**) and alcohol namely 5-(4-hydroxybutan-2-yl)-2-methylcyclohex-2-enone (**24**) by aldehyde hydrogenation. Small extents of isomerized and hydrogenated carvone (**25**) products were also observed (**Scheme-VI**).



Scheme-VI: Hydroformylation of carvone

Conclusion

The hydroformylation of various terpenes was performed using modified and unmodified Rh, Pt and Co complexes. It was observed that Wilkinson's catalyst only hydroformylate terpenes having terminal double bonds and shows poor activity. The hydroformylation of terpenes and in particular camphene was efficiently catalyzed by $Rh(CO)_2(acac)/P(OPh)_3$ catalyst system. This catalyst was more efficient for hydroformylation of terpenes, as compared to Wilkinson complex. The $Rh(CO)_2(acac)/P(OPh)_3$ catalytic system was found to give the highest activity (TOF = 417 h^{-1}) and selectivity (~ 100 %) to aldehyde for hydroformylation of camphene. The product selectivity was slightly more towards *endo* diasteriomers. The role of solvent, temperature, various phosphite ligands, P/Rh ratio and effect of temperature on the activity and selectivity of hydroformylation of camphene has been investigated. The $Rh(CO)_2(acac)/P(OPh)_3$ catalyst system is also an efficient catalyst for hydroformylation of limonene, carvone and β-pinene in addition to camphene.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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