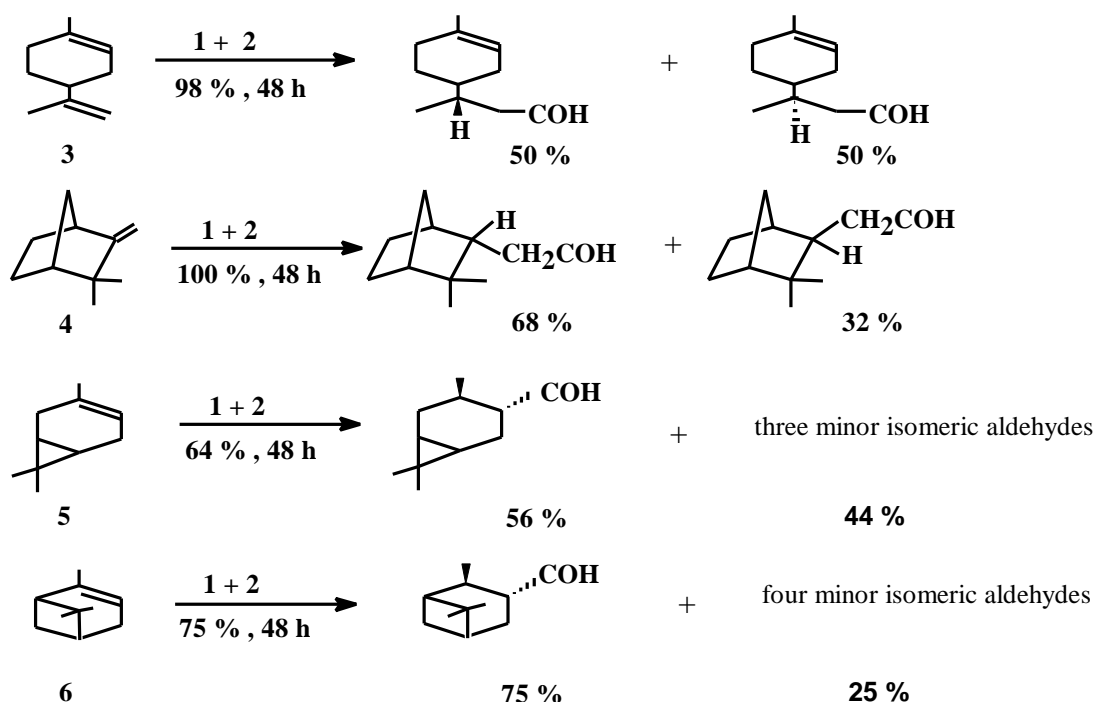


## Preparative Hydroformylation of Naturally Occurring Monoterpenes on Rh(I) Homogeneous Catalysts Modified by Auxiliary Bulky Phosphites

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Hydroformylation of naturally occurring olefinic monoterpenes seems to be a promising synthetic procedure to obtain aldehydes, which are of interest as fragrances, chiral synthons, and precursors of herbicides and chiral ligands. However, low reactivity as well as isomerization of initial monoterpenes, and poor regio- and stereoselectivity of reaction considerably decay the value of this approach. Triarylphosphites with bulky *ortho*-substituents P(O-*o*-*tert*-Bu-C<sub>6</sub>H<sub>3</sub>-*p*-R)<sub>3</sub> (**1a-c** with H, Et or *t*-Bu *para*-substituents) were suggested to be the beneficial tool for promotion the reactivity of the sterically hindered monoterpenes. Here we report, that RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> (**2**) as a catalyst precursor with added bulky phosphites, affords the efficient hydroformylation of cyclic monoterpenes with disubstituted or trisubstituted exocyclic as well as endocyclic double bonds.



Carbonylation of limonene (**3**), camphene (**4**), 3-carene (**5**), and  $\alpha$ -pinene (**6**) proceeds under mild conditions (70-110 °C, 20-90 bar of syngas in toluene solution or in neat terpene) and gives the target aldehydes in high or quantitative yields. The latter are *ca.* one order of magnitude higher than those obtained with conventional phosphine-modified rhodium(I) catalysts. When, *e.g.*, **1a+2** was used as a catalyst in hydroformylation of **5** ( molar ratio terpene/**1/2**=400/10/1, 48 h at 110 °C in toluene solution), the 64 % conversion of terpenic substrate was observed. Under these conditions only 5 % conversion of **5** was obtained for triphenyl phosphine-modified catalyst **2**. The even better results were observed for **1b** and **1c**, when these were used as the auxiliary ligands. In addition, the aldehydes obtained were shown to be useful substrates in preparing the variety of chiral products: amines, oximes, hydrazones, N-containing heterocycles and bidentate ligands.