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SELECTIVE CONVERSION OF PINANE INTO β-PINENE CATALYZED BY AN IRIDIUM PENTAHYDRIDE COMPLEX

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Summary

Pinane was catalytically converted into β-pinene with high selectivity by means of a soluble iridium pentahydride complex at 100 °C in the presence of 3,3-dimethylbut-1-ene as hydrogen acceptor.

Introduction

Finding a system which would result in an efficient selective catalytic functionalization of unreactive substrates such as the activation of the C–H bond of saturated hydrocarbons by soluble transition metal complexes is of current interest. Felkin et al. [1] recently reported that the selective catalytic conversion of methylcyclohexane into methylenecyclohexane at 100 °C can be effected using the soluble iridium pentahydride, $IrH_5(i\text{-}Pr_3P)_2$, as the catalyst, and an olefin as hydrogen acceptor. This selective catalytic reaction, which has been proved to attack preferentially the methyl group in saturated hydrocarbons, might have some useful applications in the selective functionalization of methyl group in certain organic compounds.

β-Pinene is an important intermediate in the synthesis of many chemicals. The only convenient method to obtain β-pinene is the prolonged fractional distillation for the complete separation from the isomeric α-pinene. The difficulty lies in the fact that the content of β-pinene present in nature is considerably lower than that of α-pinene as a rule, and in the tendency of β-pinene to isomerize into α-pinene during separation [2].

In order to achieve the desired counter-thermodynamic transformation of the more stable internal olefin into its less stable terminal isomer, a thermal rearrangement of the hydroboration product of α-pinene followed by displacement of β-pinene by a second alkene [3,4], a photochemical method of synthesis of β-pinene from α-pinene [5] and a two-step isomerization of α-pinene with allyltin compounds [6] have been described.

Here, we wish to report the selective catalytic conversion of pinane into β-pinene by means of a soluble iridium pentahydride complex in the presence of 3,3-dimethylbut-1-ene as the hydrogen acceptor.

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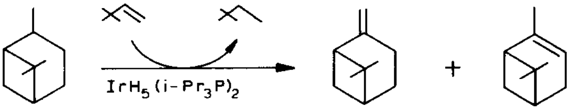
Results and discussion

When pinane, which is easily obtained from α-pinene by hydrogenation, was treated with iridium pentahydride, $IrH_5(i\text{-}Pr_3P)_2$, at 100–110 °C in the presence of 3,3-dimethylbut-1-ene as hydrogen acceptor, the products obtained are as shown below:



Conditions	Turnover numbers	Mole%	Mole%
100 °C, 10 min	8.5	97.6	2.4
30 min	10.0	93.8	6.2
1 h	12.0	89.7	10.3
4 h	11.8	77.2	22.8

The olefins were characterized by NMR, GC-MS, GC-IR spectroscopy. The proportion of the olefins in the mixture was determined by GC.

The dehydrogenation of the pinane was rapid and almost complete within one hour under the above conditions. Ten minutes after initiation, 4.0 mole% of β-pinene and 0.1 mole% of α-pinene compared to pinane were formed (turnover number of 8.5) with high regioselectivity of β-pinene (> 95%). After 1 h, the kinetic mixture of products formed contained 5.2 mole% of β-pinene (turnover number of 12.0) and 0.6 mole% of α-pinene. The latter was formed from the isomerization of β-pinene in the same catalytic system, and was proved by a control experiment. No ring-opened product was detected, even though the reaction was carried out in the presence of a small amount of acid.

It has been suggested that the catalytic dehydrogenation may proceed via a mechanism proposed by Felkin [7] in which the key step involves the insertion of a ligand-deficient intermediate into a C–H bond of the pinane methyl group. Radical and carbocationic intermediates were excluded because neither a ring-opened, nor a Wagner–Meerwein rearrangement product was detected.

The dehydrogenation of pinane could also be carried out in suitable solvents such as hexamethyldisiloxane to give the β-pinene with lower conversions (turnover number of 2–3).

Unlike the iridium system, the selective conversion into β-pinene was not affected by other transition metal systems. Almost no reaction took place when $RhH(Ph_3P)_4$, $ReH_7(Ph_3P)_2$ or $ReH_7(i\text{-}Pr_3P)_2$ were used as the catalyst, while α-pinene and ring-opened products were mainly obtained when the $PdCl_2$ system [8] was used.

To our knowledge, the conversion of pinane into β-pinene by a soluble transition metal catalyst is the first attempt to obtain the useful organic compound by activation and functionalization of a saturated hydrocarbon. Although the turnover number is not large enough, the reaction does have the potential to be applied in the activation and functionalization of the C–H bond in saturated hydrocarbons, in the future.

Experimental

All reactions were carried out under prepurified nitrogen using Schlenk techniques. The complexes $IrH_5(i\text{-}Pr_3P)_2$ [9], $ReH_7(i\text{-}Pr_3P)_2$ [10], and $ReH_7(Ph_3P)_2$ [11] were prepared by published methods. Pinane was obtained by the hydrogenation of the α-pinene under 50 atm at 150 °C by use of Raney Ni as the catalyst. After the hydrogenated products had been fractionally distilled using a 251 auto-annular still, pinane (99.7% as determined by GC) was obtained and determined using a Perkin–Elmer Sigma 2000 GC Instrument with a polyethylene glycol column. The reaction products were separated by preparative gas chromatography and characterized by NMR, IR and MS spectroscopy. ^1H NMR spectra were recorded on a Varian EM-360 or Varian XL-200 spectrometer. GC-IR spectra were recorded on a Digilab FTS-20E spectrometer. Mass spectra were recorded on a Finnigan 4021 GC/MS/DC Instrument.

Typical procedure for the dehydrogenation of pinane to give β-pinene

Pinane (8.04 mmol) was heated with $IrH_5(i\text{-}Pr_3P)_2$ (0.038 mmol) and 3,3-dimethylbut-1-ene (1.55 mmol) at 100 °C for 10 min, the red solution which formed was cooled and the conversion and selectivity were determined by GC on a column of 10% polyethylene glycol supported on 102 silanized white support. The colorless liquid obtained after distillation was used for characterization. GC-IR spectra at 879, 1643, 2920, 3078 cm^{-1} indicated the presence of β-pinene, GC-MS, m/z: 136 (M^+), 121, 93, 79, 69, 41. ^1H NMR of β-pinene was determined after separation by preparative gas chromatography. ^1H NMR ($CDCl_3$, 200 MHz): 0.72 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.31–2.60 (m, 8H) 4.60 (m, 2H, $H_2C{=}C$).

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