Selective estragole to *trans*-anethole isomerization in ionic liquids

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INTRODUCTION

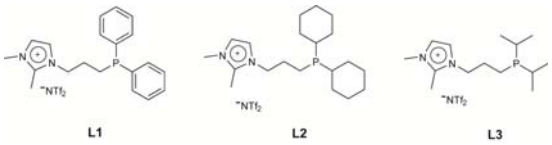
Trans-anethole is a naturally-occurring product which has been traditionally extracted from anise or fennel oils, albeit with variable proportions of its *cis*-isomer as an impurity.[1] However, the increasing demand of *trans*-anethole has made extraction from natural sources not sufficient to supply the market, hence the need to produce it synthetically.[2] Effectively, only *trans*-anethole is interesting for industry since the *cis*-isomer presents a higher toxicity and unpleasant organoleptic properties. Consequently, the search for efficient and selective catalytic systems able to promote the estragole to *trans*-anethole isomerization still remains a challenge for synthetic chemists.

RESULTS AND DISCUSSION

Initially, the catalytic activity of complexes $PdCl_2(NCPh)_2$ (**1a**), $RhCl(PPh_3)_3$ (**1b**) and $RuHClCO(PPh_3)_3$ (**1c**) in the isomerization of estragole has been tested. Experiments were performed at 80 °C using 2 mmol of substrate, 0.020 mmol of complex, 0.5 mL of toluene (**1a** and **1c**) or ethanol (**1b**), and the reaction was monitored by GC analyses of aliquots. The best results were obtained with **1c** which quantitatively converted estragole into anethole in 1 h with selectivity in the *trans* isomer of 95%. We next investigated how the process is affected by changing the catalyst loading. We observed that decreasing the amount of ruthenium (complex **1c**) from 0.020 to 0.015 mmol did not modify the *trans*:*cis* ratio (95:5). On the other hand, lower metal loadings (0.010 mmol) conduced to lower selectivities in the desired *trans*-isomer (92%). In an attempt to improve the selectivity, the process has been carried out at lower temperature (35 °C) with the most active complex **1c**. The *trans*-selectivity decreased (81% vs. 95%) and the reaction time dramatically increased (7 h vs. 1 h). The isomerization of estragole has also been tested in different amounts of toluene (0.5, 1.0 and 4.0 mL). Remarkably, complete conversion in only 5 min was observed when 0.5 mL of toluene was employed, with high selectivity in *trans*-anethole (98%).

The next step was the employment of ionic liquids in the estragole isomerization in order to obtain a simple separation of products from the reactional media. Experiments were performed at 80 °C using 2 mmol of substrate, 0.015 mmol of **1c**, 0.5 mL of toluene and 0.5 mL of $BMI{\cdot}NTf_2$. A conversion of 99% was obtained after 20 min with *trans*-selectivity of only 87%. Then, ionophilic ligands (Figure 1) were applied in this system to support the catalyst in the ionic phase and allow its recyclability.

Figure 1. Ionophilic ligands employed in isomerization.



The system containing only $BMI{\cdot}NTf_2$ has decreased its conversion by reuse of catalytic phase (99% 1st cycle; 50% 2nd cycle; 32% 3th cycle; 22% 4th cycle), although the selectivity in *trans*-anethole remains unchanged (87%). Gratifyingly, the system containing the ionophilic ligands (**L1**, **L2** or **L3**) could be re-used up to three consecutive runs without loss of conversion (>99.5%) and selectivity (96%). However, a decrease of the conversion (>99.5% vs. 91%), accompanied by a slight loss of the *trans*-selectivity (96% vs. 91%), was observed after the fourth cycle.

CONCLUSION

In summary, the $RuHClCO(PPh_3)_3$ has shown to be effective catalyst to convert estragole into anethole. The best conversion (>99.5%) and selectivity toward *trans*-anethole (98%) were obtained with 0.015 mmol of this precursor, 0.5 mL of toluene, 80 °C and 5 min of reaction. Furthermore, the system containing $BMI{\cdot}NTf_2$ and ionophilic ligands showed to be a good alternative to recycle the catalyst with high conversions (>99.5%) and high *trans*-selectivities (96%).

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