

Hydroaminomethylation of 1-Dodecene Catalyzed by Water-soluble Rhodium Complex

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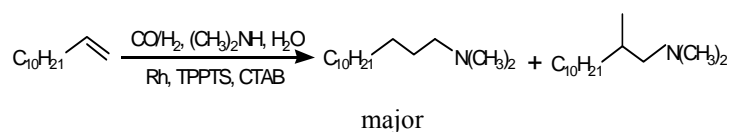
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Abstract: The hydroaminomethylation of 1-dodecene catalyzed by water soluble rhodium complex $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ in the presence of surfactant CTAB was investigated. High reactivity and selectivity for tertiary amine were achieved under relatively mild conditions.

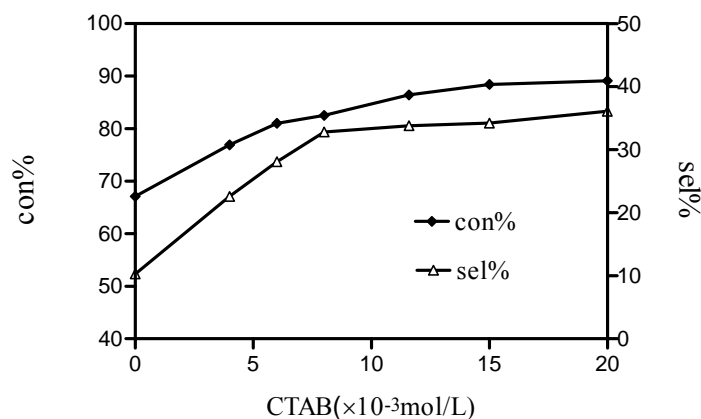
Keywords: Hydroaminomethylation, 1-dodecene, water-soluble rhodium complex, biphasic catalytic system.

The hydroaminomethylation of olefin to form an amine represents an atom-economic efficient, and most elegant synthesis of amine compounds. Homogeneous catalysis of this reaction has been continuously improved and optimized since it was discovered in 1949 by Reppe and co-workers¹. In order to overcome the difficulty of catalyst separation and improve catalyst activity, Herwig *et al.*² investigated the hydroaminomethylation of lower olefins ($\leq \text{C}5$) in water-organic two-phase system, and achieved high conversion and selectivity. However, to our knowledge, the catalytic hydroaminomethylation in water-organic two-phase has not been extended to relatively water-insoluble long chain olefins in spite of the highly industrial importance of the resulting long chain aliphatic tertiary amines, from which the cationic and zwitterionic surfactants can be prepared and widely used in petrochemical, agrochemical and pharmaceutical industries³. We report here the preliminary results of catalytic hydroaminomethylation of 1-dodecene with dimethylamine in aqueous biphasic system using $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ [TPPTS: $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$] as a water-soluble catalyst in the presence of surfactant cetyltrimethylammonium bromide (CTAB).

Scheme 1 Hydroaminomethylation reaction of 1-dodecene

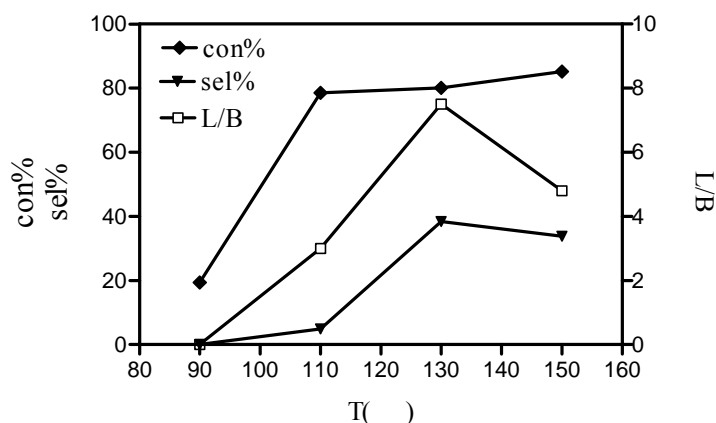


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Figure 1 Influence of CTAB concentration on hydroaminomethylation of 1-dodecene

RhCl(CO)(TPPTS)₂ $1.8 \times 10^{-3} \text{ mol/L}$; TPPTS $5.4 \times 10^{-2} \text{ mol/L}$; P:Rh=32:1; dimethylamine: dodecene = 8:1; CO:H₂=1:1; P=3 MPa; T=130 °C; t=5 h

The hydroformylation of 1-dodecene nearly did not occur in the absence of surfactants in the biphasic catalytic system because of its very low solubility in water, but addition of cationic surfactants could enhance the reaction rate dramatically⁴. We envisioned that the addition of a surfactant would also favor the hydroaminomethylation of 1-dodecene. The results (**Figure 1**) showed that hydroaminomethylation of 1-dodecene in the absence of cationic surfactant CTAB was only with a 67% conversion. But the addition of CTAB did accelerate the reaction apparently in the micellar solution. This can be attributed to that the formation of micelle expanded the interfacial area between aqueous and organic phases and enriched the concentration of rhodium catalyst in the interface layer by means of the static electrostatic attraction of micelle with anionic rhodium active species⁵.

Figure 2 Influence of reaction temperature on hydroaminomethylation of 1-dodecene

RhCl(CO)(TPPTS)₂ $1.8 \times 10^{-3} \text{ mol/L}$; TPPTS $5.4 \times 10^{-2} \text{ mol/L}$; P:Rh=32:1; dimethylamine:dodecene = 8:1; CTAB 0.01 mol/L; CO:H₂=1:1; P=3 MPa; t=5 h; L/B: the ratio of linear to branched tertiary amine

The effect of temperature on hydroaminomethylation is shown in **Figure 2**. When the temperature rose from 90°C to 150°C, the conversion of 1-dodecene was significantly increased from 20% to 85%, while the selectivity for tertiary amine and the regioselectivity for linear tertiary amine decreased when the temperature was over 130°C, that might result from the reduction of solubility of syngas and gaseous dimethylamine in solution, or from ligand degradation at higher temperature.

At lower concentration of rhodium catalyst, the hydrogenation side reaction was evident (**Table 1**). With the catalyst concentration increased, the selectivity for tertiary amine increased continuously till to about 85%. Under the conditions, lengthening the reaction time to 12 hours, 91.4% conversion of 1-dodecene and 83.9% selectivity for tertiary amine were achieved.

Table 1 Influence of rhodium concentration on hydroaminomethylation of 1-dodecene^a

entry	concentration of rhodium	dodecane %	isomerized dodecene %	aldehyde%		amine%		con%	sel% (amine)	L/B ^b (amine)
				L	B	L	B			
1	0.5×10^{-3}	31.0	13.0	24.7	13.0	6.1	2.4	89.0	8.3	2.5
2	1.8×10^{-3}	24.1	10.9	7.5	8.0	28.7	4.1	83.1	39.4	7.2
3	2.7×10^{-3}	16.5	8.0	2.2	6.2	42.4	5.6	80.9	59.4	7.5
4	3.6×10^{-3}	14.5	7.5	1.6	4.0	45.9	5.9	74.0	62.5	7.8
5	5.4×10^{-3}	8.0	4.9	1.3	3.4	54.5	5.7	77.8	77.4	9.6
6	10×10^{-3}	7.4	5.5	0.6	0.9	65.2	4.8	84.5	82.9	13.4
7 ^c	10×10^{-3}	8.1	5.9	0.4	0.4	70.4	6.3	91.4	83.9	11.3

a. Reaction conditions are the same as in **Figure 2**; b. L: linear, B: branched; c. t=12 h

Acknowledgments

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