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THE PLATINUM COMPLEX CATALYZED TRANSFORMATION OF PRIMARY AMINE TO SECONDARY AMINE

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Platinum complex combined with $SnCl_2 \cdot 2H_2O$ activates a primary amine and catalyzes the transformation to the secondary amine at 180 °C. Dibutylamine was obtained from butylamine in 74% yield.

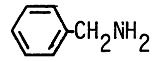
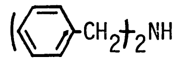
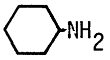
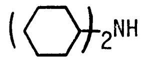
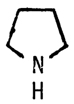
Although intensive researches have been performed with Group VIII first and second row transition metal catalysts in wide variety of reactions, few attention has been paid to a homogeneous platinum catalysis. There are only several specific examples, in which homogeneous platinum complex shows high catalytic activity.$^{1)}$ Such rarity of high activity seems to be caused by the fact that an intermediate platinum complex is generally stable,$^{2a,b)}$ and the catalytic cycles may cease at the stage including those stable species.

In this letter, we wish to describe a novel catalysis of homogeneous platinum complex. The homogeneous platinum catalyst activates a primary amine and catalyzes the transformation to a secondary amine. The same reaction is reported to be catalyzed by ruthenium$^{3a,b)}$ and palladium$^{4)}$ catalysts.

A mixture of a primary amine (20 mmol), $PtCl_2(PPh_3)_2$ (0.10 mmol, 0.5 mol% based on the primary amine charged), $SnCl_2 \cdot 2H_2O$ (0.25 mmol), and benzene (10 ml) was stirred in a stainless steel reactor at 180 °C for 5 h.

Some representative results are listed in Table 1. The reaction did not proceed at all in the absence of $SnCl_2 \cdot 2H_2O$. The yield of dibutylamine showed a maximum at 2.5 of Sn/Pt ratio (Run 2). Employment of other Lewis acids such as $SnCl_4$, $FeCl_3$, or $AlCl_3$ in place of $SnCl_2 \cdot 2H_2O$ was not favorable for this reaction. Tin(II) chloride must be operative as a supplier of $SnCl_3^-$ ligand as investigated fully by H. C. Clark and co-workers$^{5a-d)}$. Elimination of a phosphorus ligand from the catalyst system slightly reduced the yield of the secondary amine (Run 3). However, addition of $Ph_2P(CH_2)_2PPh_2$ (P/Pt=2.5) to $Pt(PhCN)_2Cl_2$-$2.5SnCl_2 \cdot 2H_2O$ system reduced the yield drastically. The secondary amine was not obtained at all when tributylphosphine or triphenylphosphite (P/Pt=2.5) was used as the phosphorus ligand. The reaction proceeds readily in benzene, whereas donor solvents such as dioxane, THF, or acetonitrile suppressed the reaction. This procedure is applicable to other primary amines (Runs 5-7).

Table 1. Platinum Complex Catalyzed Transformation of Primary Amine to Secondary Amine[a)]

Run	Primary amine	Sn/Pt	Product	
			Secondary amine	Yield/% [b)]
1	$CH_3CH_2CH_2CH_2NH_2$	1.5	$(CH_3CH_2CH_2CH_2)_2NH$	27
2	$CH_3CH_2CH_2CH_2NH_2$	2.5	$(CH_3CH_2CH_2CH_2)_2NH$	74[c)]
3[d)]	$CH_3CH_2CH_2CH_2NH_2$	2.5	$(CH_3CH_2CH_2CH_2)_2NH$	65
4	$CH_3CH_2CH_2CH_2NH_2$	5.0	$(CH_3CH_2CH_2CH_2)_2NH$	64
5		2.5		81(90)
6		2.5		59(84)
7[e)]	$H_2N(CH_2)_4NH_2$	2.5		8(89)

a) Primary amine (20 mmol), $PtCl_2(PPh_3)_2$ (0.10 mmol), $SnCl_2\ 2H_2O$ (0.25 mmol), benzene (10 ml), at 180 °C, for 5h.

b) By GLC. Figures in parentheses are selectivities to the secondary amines.

c) Tributylamine was also obtained in 8% yield.

d) $PtCl_2(PhCN)_2$ (0.10 mmol) in place of $PtCl_2(PPh_3)_2$.

e) Diamine (10 mmol) was used without solvent.

This reaction appears to include the formation of an imine intermediate and the nucleophilic attack of the primary amine to the imine intermediate followed by elimination of ammonia.[3,4)]

References

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