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PLATINUM COMPLEX CATALYZED TRANSFORMATION OF AMINE.[1] N-ALKYLATION AND N-ALLYLATION USING PRIMARY ALCOHOLS

Yasushi TSUJI, Ryo TAKEUCHI, Hiroshi OGAWA, and Yoshihisa WATANABE*
Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606

Amines reacted with primary alcohols in the presence of a platinum complex catalyst at 120-180 °C to give N-alkylated or N-allylated compounds.

Recently, intensive researches have been carried out on Ru or Pd catalyzed transformation of amines including N-alkylation [3a] and N-allylation [3b] with alcohols as well as transalkylation.[4] However, Pt catalyzed transformation has attracted a little attention.[2] In this letter, we wish to report a novel catalysis of homogeneous platinum complex, which mediates N-alkylation and N-allylation of amines with primary alcohols.

Some representative results of N-alkylation are shown in Table 1. Aniline reacted with ethanol in the presence of $PtCl_2(PhCN)_2$ and $SnCl_2 \cdot 2H_2O$ as catalyst to give N,N-diethylaniline in high yield (Run 1). Without $SnCl_2 \cdot 2H_2O$ (Run 2) or with triphenylphosphine ligand (Run 3), conversion of aniline was low and N-monoalkylanilines were obtained in only low yields. The reaction can be controlled at the N-monoalkyation stage (Run 4). Aliphatic amines were also N-alkylated in high yields without transalkylation reactions (Run 5), which were often significant side reactions with Ru catalyst.[4] Similar reaction using allylic alcohols gave N-allylated products (Scheme 1). The reaction was carried out at 120 °C for allyl alcohol(**1**) or at 150 °C for crotyl(**2**) and methallyl(**3**) alcohols in the presence of $PtCl_2(PPh_3)_2$ (0.5 mol% based on the amines) and $SnCl_2 \cdot 2H_2O$ (Sn/Pt=0.5) as catalyst. This catalysis of Pt complex is quite different from that of Ru.[5] $RuCl_2(PPh_3)_3$ (1 mol% based on the amine) catalyzed the N-heterocyclization to give quinolines in high yields (Eq. 1),[5] while with Pt catalyst such a N-heterocyclization did not take place at all. In separate experiments, the present Pt catalyst system did not catalyze an isomerization of the allylic alcohols to the corresponding aldehydes, while $RuCl_2(PPh_3)_3$ did. This different feature between Pt and Ru might cause the different catalytic ability, because the N-heterocyclization proceeds via isomerisation of allylic alcohols to corresponding aldehydes.[5]

Table 1. Platinum Catalyzed N-Alkylation using Alcohols [a]

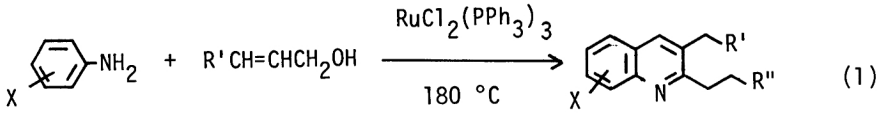
Run	$R\text{-}NH_2$	R'OH	Sn/Pt	Conv. of $R\text{-}NH_2$/% [b]	Yield/% [b] $R\text{-}NR'_2$	$R\text{-}NHR'$
1	$PhNH_2$	EtOH	0.5	100	82	4
2	$PhNH_2$	EtOH	0	13	0	2
3[c]	$PhNH_2$	EtOH	0.5	38	0	trace
4[d]	$PhNH_2$	n-BuOH	1.0	90	2	85
5[e]	$n\text{-}C_8H_{17}NH_2$	n-BuOH	0.6	95	90	0
6	$n\text{-}C_8H_{17}NH_2$	n-BuOH	1.1	97	14	58

a) Amine(20 mmol), alcohol(10 ml), $PtCl_2(PhCN)_2$(0.2 mmol), $SnCl_2\cdot 2H_2O$ at 180 °C for 4 h. b) Determined by GLC. c) $PtCl_2(PPh_3)_2$(0.2 mmol). d) At 150 °C for 1.3 h. e) Alcohol(20 ml).

$$R\text{-}NH_2 + R'CH{=}CHR''CH_2OH \xrightarrow[120\ °C\text{-}150\ °C]{PtCl_2(PPh_3)_2\text{-}SnCl_2\cdot 2H_2O} R'CH{=}CHR''CH_2NHR$$

R=Ph	R'=R''=H	(1)	67%
R=Ph	$R'=CH_3$, R''=H	(2) (E=100%)	64% (E/Z=3/1)
R=Ph	R'=H, $R''=CH_3$	(3)	84%
$R=n\text{-}C_8H_{17}$	R'=R''=H	(1)	57%

Scheme 1.



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