CHEMISTRY LETTERS, pp. 293-294, 1986.

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)]

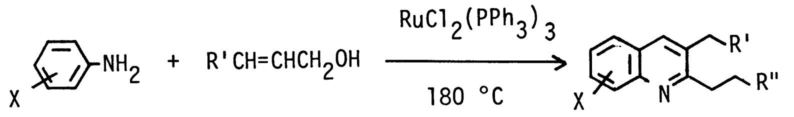
Run	$R\text{-}NH_2$	R'OH	Sn/Pt	Conv. of $R\text{-}NH_2$/% [b)]	Yield/% [b)]	
					$R\text{-}NR'_2$	R-NHR'
1	$PhNH_2$	EtOH	0.5	100	82	4
2	$PhNH_2$	EtOH	0	13	0	2
3[c)]	$PhNH_2$	EtOH	0.5	38	0	trace
4[d)]	$PhNH_2$	n-BuOH	1.0	90	2	85
5[e)]	$n\text{-}C_8H_{17}NH_2$	n-BuOH	0.6	95	90	0
6	$n\text{-}C_8H_{17}NH_2$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

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

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.



(1)

References

1) Part II in a series of "Platinum Complex Catalyzed Transformation of Amine." For the Part I, see Ref. 2 .

2) Y. Tsuji, J. Shida, R. Takeuchi, and Y. Watanabe, Chem. Lett., 1984, 889.

3) a) Y. Watanabe, Y. Tsuji, H. Ige, Y. Ohsugi, and T. Ohta, J. Org. Chem., 49, 3359 (1984), and references cited therein; b) K. E. Atkins, W. E. Walker, and R. M. Manyik, Tetrahedron Lett., 1970, 3821.

4) R. B. Wilson, Jr. and R. M. Laine, J. Am. Chem. Soc., 107, 361 (1985).

5) Y.Watanabe, Y. Tsuji, Y. Ohsugi, and J. Shida, Bull. Chem. Soc. Jpn., 56, 2452 (1983).

(Received November 27, 1985)