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$WCl_6/LiAlH_4$ PROMOTED TRANSFORMATION OF IMINES INTO SECONDARY AND TERTIARY AMINES

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Summary

The reaction of $WCl_6/LiAlH_4$ with imines, R'N=CHR, gave tertiary amines, $R'N(CH_2R)_2$, and secondary amines, $R'NHCHRCH_2R$. Isotope labeling experiments revealed that the reaction involved two types of azatungstenacyclobutanes, WNR'CHRCHR and WCHRNR'CHR, produced from the reaction of an alkylidene tungsten intermediate with the imine C=N double bond. Formation of these metallacyclobutanes is highly dependent on the solvent used.

Introduction

The mechanism of olefin metathesis has been extensively investigated and now it is generally accepted that the reaction proceeds by a stepwise mechanism involving alternating alkylidenemetal and metallacyclobutane intermediates [1]. On the other hand, the proposed intermediates, alkylidenemetals, have been trapped by unsaturated molecules such as olefins [2] and carbonyl compounds [3] to give cyclopropane derivatives and methylene transfer products such as Wittig type products, respectively. Recently Schrock reported that alkylidenetantalum complexes smoothly reacted with imines to provide new alkylimidotantalum complexes and olefins [4]. Furthermore, Hegedus has shown that carbenechromium complexes react under sunlight with imines to produce β-lactams in good yields, where an azachromiacyclobutane intermediate is suggested [5].

These results suggest that some catalytic systems could promote a transformation reaction of imines similar to olefin metathesis into olefins and azo compounds or some other nitrogen-containing compounds. In this regard we wish to report herein that the reaction of the $WCl_6/LiAlH_4$ system, with imines **1a–1f** produces tertiary

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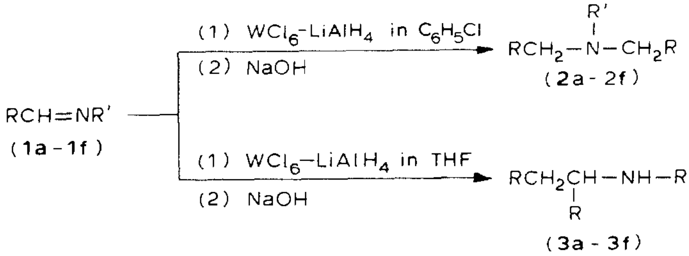
amines **2a–2f** and secondary amines **3a–3f** after hydrolysis, where azatungstenacyclobutanes may be involved as possible intermediates.



(1)

Results and discussion

The $WCl_6/LiAlH_4$ system, which is known to exhibit high catalytic activity for olefin metathesis and promotes reductive coupling reactions of carbonyl compounds providing olefins [6], has been found to promote a reaction of imines as shown in eq. 1. The combination of WCl_6 and $LiAlH_4$ is required for formation of amines after hydrolysis and the optimum molar ratio: $WCl_6/LiAlH_4$/imine is 1/1/4. The representative results obtained from the reaction of $WCl_6/LiAlH_4$ with imines are shown in Table 1. Although the reaction did not occur catalytically it was found that the reaction products were significantly dependent upon the solvent used. In chlorobenzene benzaldehyde N-substituted imines **1a–1c** produced the tertiary amines **2a–2c** as main products in good yields. However imine **1d** which has a bulkier substituent on nitrogen provided secondary amine **3d** as the main product even in chlorobenzene with a trace amount of tertiary amine **2d**. On the other hand, in THF secondary amine **3a** or **3b** is produced as a main product in a poor yield with contamination of a hydrogenated product, $R'NHCH_2Ph$ [7].

In order to clarify the reaction mechanism a reaction with $LiAlD_4$ was carried out. When $LiAlD_4$ was used in place of $LiAlH_4$ the reaction of **1a** in chlorobenzene gave

TABLE 1

REACTION OF $WCl_6/LiAlH_4$ WITH IMINES

Imine (RCH=NR′) (1)		Solvent	Product (%) [a]	
			$RCH_2\overset{\overset{R'}{\vert}}{N}CH_2R$ (2)	$RCH_2\overset{\overset{R}{\vert}}{C}HNHR'$ (3)
PhCH=NEt	(**1a**)	C_6H_5Cl	53	–
PhCH=N-n-Bu	(**1b**)	C_6H_5Cl	67	–
PhCH=NPh	(**1c**)	C_6H_5Cl	69	–
PhCH=N-t-Bu	(**1d**)	C_6H_5Cl	trace	5
$(CH_3)_2$CHCH=N-n-Bu	(**1e**)	C_6H_5Cl	39	–
PhCH=NEt	(**1a**)	THF	–	10
PhCH=N-n-Bu	(**1b**)	THF	–	7
p-MeC_6H_4CH=N-n-Bu	(**1f**)	THF	–	12

[a] GLC yield based on WCl_6.

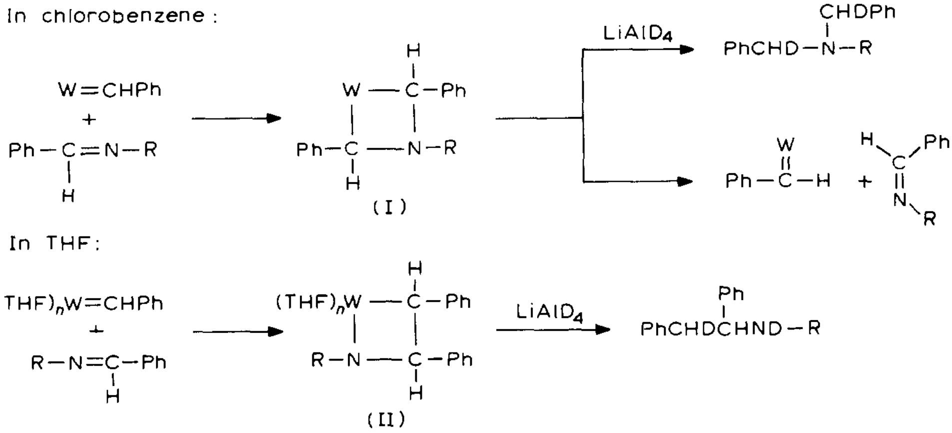
2a-d_2, $(PhCHD)_2NEt$ (eq. 2), which was identified by its NMR and mass spectra. Furthermore, evidence that another intermediate is involved in the same reaction in THF was provided by isolation of PhCHDCHPhNH(D)Et from the reaction of imine **1a** with $WCl_6/LiAlD_4$ in THF (eq. 3). These results seem to indicate that as

$$PhCH{=}NEt \xrightarrow[C_6H_5Cl]{WCl_6/LiAlD_4} (PhCHD)_2NEt \tag{2}$$

$$PhCH{=}NEt \xrightarrow[THF]{WCl_6/LiAlD_4} PhCHDCHPhNH(D)Et \tag{3}$$

shown in Scheme 1 the reaction proceeds through an azatungstenacyclobutane

SCHEME 1



intermediate such as I or II, which might be generated from attack of imine on alkylidene metal in a similar fashion to the olefin metathesis reaction [1]. Subsequent hydrogenolysis of these metallocyclobutanes with $LiAlH_4$ ($LiAlD_4$) gave the corresponding amines.

Alternatively, it would be possible that the hydrogenated product, $PhCH_2NHEt$, adds to the starting imine followed by deamination to provide the tertiary amine. A similar mechanism has appeared in $RuCl_2(PPh_3)_3$ catalyzed secondary and tertiary amine formation reactions from primary amines [8]. This alternative pathway can be ruled out in view of the result that the addition of $PhCH_2NHEt$ to the reaction mixture of $WCl_6/LiAlH_4$/imine in chlorobenzene did not increase the formation of a tertiary amine.

Generally, the M=C double bond in alkylidenemetal complexes should be polarized depending upon several factors such as the oxidation state of the metal and the electronic property of the ligand including oxo and halide ligands as shown in eq. 4 [1b,9].

$$\underset{\textbf{(4a)}}{M^+\text{-}C^-HR} \leftrightarrow \underset{\textbf{(4)}}{M{=}CHR} \leftrightarrow \underset{\textbf{(4b)}}{M^-\text{-}C^+HR} \tag{4}$$

Our results obtained here can be explained in terms of a change in polarization of the M=C double bond caused by coordination of solvent and steric interaction in an azametallacyclobutane. In chlorobenzene the imine nitrogen should add to the electrophilic carbene carbon as in the Fischer-type alkylidene complexes **4b**, while in THF the alkylidenetungsten complex coordinated by THF might be attacked in the opposite direction like the Schrock-type alkylidene complexes **4a** [4]. The facts that imine **1d** gave the secondary amine as the main product even in chlorobenzene and that the reactivity of **1d** or **1e** became low can be explained by the steric effect in the azatungstenacyclobutane intermediate.

Furthermore, as can be seen in Fig. 1 it was found that upon addition of PPh_3 to the reaction mixture the formation of a secondary amine was observed even in chlorobenzene with decreasing amount of a tertiary amine. The maximum yield of the secondary amine was obtained upon addition of one equivalent of PPh_3. Since the PPh_3 ligand could coordinate to the central metal, the azatungstenacyclobutane containing PPh_3 would be a more favorable intermediate as reaction intermediate II in THF.

In our reaction system WCl_6 alone is not reactive for the transformation of imines, and addition of $LiAlH_4$ causes the reaction, suggesting that WCl_6 is reduced by $LiAlH_4$ to some lower valent tungsten species which would react with imine to give an alkylidene complex. Although an attempt to trap the alkylidenemetal complex failed, it is reasonable to assume that this reaction would involve an alkylidenemetal intermediate in view of the fact that iminium salts react with low-valent tungsten carbonyl complexes, $M_2W(CO)_5$ ($M = Na$ and Li), to produce the alkylidene complex, $(CO)_5W{=}CPh_2$ [10], and moreover that an alkylidenetungsten has been shown to be involved in the reaction of $WCl_6/LiAlH_4$ with carbonyl compounds [6]. An attempt to isolate an azatungstenacyclobutane complex containing THF or a phosphine ligand from our reaction system is currently under investigation.

Experimental

All manipulations were carried out under nitrogen. Imines were prepared according to the reported methods [11]. Other starting materials were of commercial grade. THF and chlorobenzene were dried by the usual method and distilled under nitrogen. WCl_6 was purified by sublimation. The MS spectrum was recorded on a Hitachi M-80 instrument.

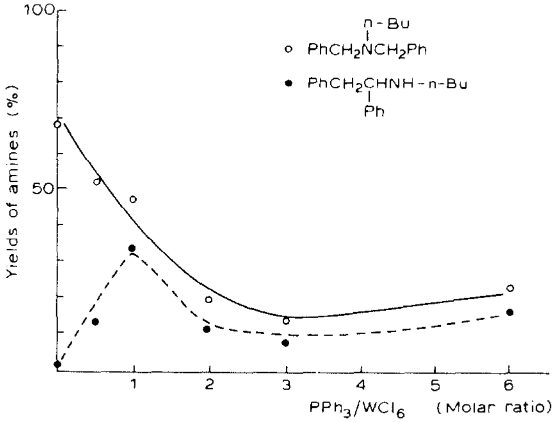


Fig. 1. Yields of tertiary and secondary amines from reaction of $WCl_6/LiAlH_4$ with $PhCH{=}N\text{-}n\text{-}Bu$ in chlorobenzene as a function of the molar ratio of added PPh_3 to WCl_6.

Reaction of WCl_6-$LiAlH_4$ with imines

The general procedure was as follows: WCl_6 (0.5 mmol) was added to 30 ml of chlorobenzene cooled to −55°C, followed by addition of $LiAlH_4$ (0.5 mmol) and then imine (2.0 mmol). Reaction took place smoothly to give a deep red solution. The reaction mixture was then warmed to room temperature and further stirred for 5 h. The reaction was quenched with 20% aqueous NaOH and organic products were extracted with ether. The yields were determined by GLC using an internal standard (stilbene), and are summarized in Table 1.

Reaction of WCl_6-$LiAlD_4$ with imine ***1a***

The reaction was carried out in a similar manner to that described above using $LiAlD_4$ instead of $LiAlH_4$. After the usual work up, the reaction products were isolated by GLC and identified by NMR and mass spectroscopy. Mass spectra for $(PhCHD)_2NEt$ (*m/e*, rel int.): 227 (M^+, 79); 212(100); 92(99), for PhCHDCHPhNH(D)Et: 227 (M^+, 7); 212(25); 134(5); 92(100).

Effect of addition of PPh_3 on the reaction of $WCl_6/LiAlH_4$ with imines

To a chlorobenzene solution of PPh_3 were added WCl_6 (0.5 mmol) and $LiAlH_4$ (0.5 mmol) at −50°C. Imine **1b** was then added dropwise. The reaction mixture was stirred for 20 h at room temperature. After the same work up as described above the product yields were determined by GLC using an internal standard. The results are shown in Fig. 1.

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