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# PALLADIUM-CATALYZED AROMATIC AMINATION OF ARYL BROMIDES WITH N,N-DIETHYLAMINO-TRIBUTYLTIN

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The reaction of N,N-diethylamino-tributyltin with aryl bromides in the presence of a catalytic amount of $PdCl_2(o\text{-}tolyl_3P)_2$ gave N,N-diethylaminobenzene derivatives. The reaction is a new kind of amination different from ones through aryne or $S_{RN}1$ mechanism

For the aromatic nucleophilic amination of general aryl bromides, the aryne-[1) and the $S_{RN}1$[2) mechanisms are known as typical examples. During the course of the investigation for the application of organotin compounds in organic synthesis, we found a novel palladium-catalyzed aromatic amination by means of N,N-diethylamino-tributyltin. In recent palladium chemistry, there is no report on palladium-catalyzed aromatic amination, although allylic amination[3) and aromatic amidation[4) were reported.

$$n\text{-}Bu_3SnNEt_2 + PhBr \xrightarrow[\text{in } PhCH_3]{PdCl_2(o\text{-}tolyl_3P)_2} PhNEt_2 + n\text{-}Bu_3SnBr$$

The reaction was carried out as follows: a stirred solution of PhBr (10 mmol), $Bu_3SnNEt_2$ (15 mmol), and $PdCl_2(o\text{-}tolyl_3P)_2$ (0.1 mmol) in toluene (5 ml) was heated under argon at 100°C for 3 h. The reaction mixture was washed with an aqueous hydrochloric acid solution and the organic layer was separated. The aqueous layer was made alkaline with sodium hydroxide. The product was extracted with ether, dried over anhydrous sodium sulfate, and isolated by distillation under reduced pressure. The results are shown in Table 1.

As shown in Table 1, $PdCl_2(o\text{-}tolyl_3P)_2$ was the best catalyst examined. Chlorobenzene and iodobenzene did not give the product. Bromobenzene, m- and p-methylbromobenzene, and p-chlorobromobenzene were better substrates, while the reaction with bromobenzene having other substituents gave rather poorer yields. The following observations show that the present reaction proceeds through neither aryne nor $S_{RN}1$ mechanism, although the addition of p-dinitrobenzene (inhibitor for $S_{RN}1$) somewhat suppressed the yield of the product. a) The products from substituted bromobenzenes did not contain the isomers constrasting with aryne mechanism. b) The reaction with iodobenzene, the best substrate for $S_{RN}1$, did not give the product.

Table 1. Pd-Catalyzed Aromatic Amination by N,N-Diethylamino-tributyltin

| Aryl Halide<br>R- $C_6H_4$ | -X | Catalyst | Yield of $RC_6H_4NEt_2$<br>(%)[a] |
|---|---|---|---|
| H- | -Br | none | (0) |
| H- | -Br | $Pd(Ph_3P)_4$ | (5) |
| H- | -Br | $PdCl_2(Ph_3P)_2$ | (7) |
| H- | -Br | $PdCl_2$(o-tolyl$_3$P)$_2$ | (87), 81, (35)[b] |
| H- | -Br | $PdCl_2$[(o-ClC$_6$H$_4$)$_3$P]$_2$ | (21) |
| H- | -I | $PdCl_2$(o-tolyl$_3$P)$_2$ | (0) |
| H- | -Cl | $PdCl_2$(o-tolyl$_3$P)$_2$ | (0) |
| o-Me- | -Br | $PdCl_2$(o-tolyl$_3$P)$_2$ | 33 |
| m-Me- | -Br | $PdCl_2$(o-tolyl$_3$P)$_2$ | 61 |
| p-Me- | -Br | $PdCl_2$(o-tolyl$_3$P)$_2$ | (80), 79 |
| p-MeO- | -Br | $PdCl_2$(o-tolyl$_3$P)$_2$ | (44), 39 |
| p-Cl- | -Br | $PdCl_2$(o-tolyl$_3$P)$_2$ | 55 |
| p-Br- | -Br | $PdCl_2$(o-tolyl$_3$P)$_2$ | (34), 30 |
| p-MeCO- | -Br | $PdCl_2$(o-tolyl$_3$P)$_2$ | 16 |
| p-$O_2$N- | -Br | $PdCl_2$(o-tolyl$_3$P)$_2$ | 24 |
| p-$Me_2$N- | -Br | $PdCl_2$(o-tolyl$_3$P)$_2$ | 36 |

a) Isolated yield based on aryl bromide, GLC yield in parentheses.

b) Addition of 10 mol% of p-dinitrobenzene.

c) The reaction with p-chlorobromobenzene did not give di-substituted product, contrasting with $S_{RN}1$. For comparison, the reaction of p-chlorobromobenzene with potassium N,N-diethylamide in diethylamine (analogous conditions to $S_{RN}1$) was carried out.

$$\begin{array}{ccccccc} KNEt_2 & + & p\text{-}ClC_6H_4Br & \xrightarrow[\text{room temp}]{\text{in } HNEt_2} & p\text{-}ClC_6H_4NEt_2 & + & C_6H_5NEt_2 \\ 2.0\text{ mmol} & & 1.0\text{ mmol} & & \text{trace} & & 13\% \end{array}$$

The major product was N,N-diethylaminobenzene, indicating intermediacy of p-N,N-diethylaminophenyl radical. The most probable mechanism for the present reaction is thought to involve the oxidative-addition, transmetalation, and reductive-elimination sequences. Further works are in progress.

## References

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