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Preliminary communication

AROMATIC SUBSTITUTION OF OLEFINS. ARYLATION WITH ANILINES VIA THE C-N BOND CLEAVAGE IN THE PRESENCE OF PALLADIUM(II) ACETATE*

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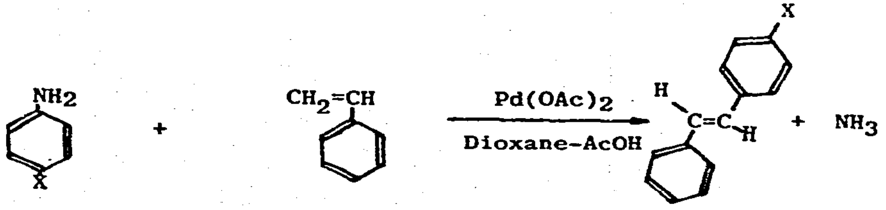
Summary

A new aromatic substitution reaction of styrene by arylamines such as aniline, _p_-toluidine, _p_-anisidine, _p_-chloroaniline, and _p_-nitroaniline in the presence of palladium(II) acetate has been found to give (E)-stilbene, (E)-_p_-methylstilbene, (E)-_p_-methoxystilbene, (E)-_p_-chlorostilbene, and (E)-_p_-nitrostilbene, respectively, in modest yields.

We have reported that the double bond of olefins undergoes substitution by suitable aromatic compounds in the presence of palladium(II) salts.[1] This reaction is now widely recognized as one of the key reactions in the coupling of olefins with aromatic compounds catalyzed by palladium complexes. We have found that primary arylamines ($Ar-NH_2$) can function as an arylating agent by C-N bond cleavage when treated with palladium



X:H, CH_3, OCH_3, Cl, NO_2

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[*] Part 26 of this series. Previous paper: ref 1c.

salts and acetic acid and report arylation reactions of styrene by aniline, *p*-toluidine, *p*-anisidine, *p*-chloroaniline, and *p*-nitroaniline. Thus, when a mixture of aniline, styrene, palladium(II) acetate (equimolar amounts of each) and acetic acid in dioxane or acetonitrile was heated at reflux for 8 hr, there was obtained a 24.5% yield of (E)-stilbene[*] (based on aniline used) together with acetanilide, 1,4-diphenylbutadiene, biphenyl, (E)-*p*-aminostilbene,[**] ammonia,[***] and metallic palladium.

Similarly, *p*-toluidine, *p*-anisidine, *p*-chloroaniline, and *p*- and *m*-nitroaniline gave the corresponding (E)-stilbene derivatives. Table I summarizes the results and shows that aniline

Table I. Formation of Stilbenes by Reaction of Anilines with Styrene[a]

Aniline	(E)-Stilbene	Yield, %[b]
Aniline	Stilbene	25[c]
Aniline	Stilbene	19[d]
p-Toluidine	p-Methylstilbene	28[e]
p-Anisidine	p-Methoxystilbene	30[e]
p-Nitroaniline	p-Nitrostilbene	11[e]
m-Nitroaniline	m-Nitrostilbene	17[e]
p-Chloroaniline	p-Chlorostilbene	40[e]

[a] Reactions were run charging aniline, styrene, and palladium acetate (1.05 mmol each) using acetic acid (1.75 ml) and dioxane (10.8 ml) as solvent with stirring at reflux for 8 hr under air.

[b] GC yield based on anilines used.

[c] Acetonitrile was the solvent.

[d] Acetanilide (64%), 1,4-diphenylbutadiene (10%), and biphenyl (trace) also were formed.

[e] Considerable amounts of the corresponding acetanilide derivatives were formed via condensation of anilines and acetic acid.

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[*] It was confirmed by control experiments that stilbene was formed in the direct reaction of aniline and styrene, and not in the reaction of styrene and acetanilide which was formed by condensation of aniline and acetic acid.

[**] Interestingly, only a trace amount of the usual aromatic substitution product, (E)-*p*-aminostilbene was formed, presumably because of the protonation of aniline by acid.

[***] Formation of ammonia was confirmed by Nessler's reagent.

derivatives can function as the arylating agent through C-N bond cleavage. The C-N bond cleavage of aniline by palladium also was confirmed by the following experiment. Bubbling of carbon monoxide at atmospheric pressure into a refluxing mixture of aniline, palladium acetate (1 mmol each), acetic acid (1.75 ml), and acetonitrile (10 ml) with stirring for 8 hr, and subsequent addition of bromine at -78°C and methanolysis furnished methyl benzoate in 16% yield.

Although the yield of stilbenes is still low*, the characterristic feature of this new reaction is that the reaction can be performed in acidic medium, in contrast to the arylation by aryl halides which is carried out under basic conditions.[2] The mechanism of this reaction, especially that of the C-N bond cleavage step, is not yet clear at this stage. Two mechanism may be considered. One involves oxidative addition of $Ph{-}NH_2$ to $Pd(0)$ to form a $Ph{-}Pd{-}NH_2$ species and the other involves a $Ph\underset{H}{N}{-}Pd^{II}OAc$ intermediate.

We believe this to be the first demonstration of arylation of olefins by aniline derivatives by way of C-N bond cleavage by palladium. Studies are currently underway to explore the scope of this new aromatic substitution of olefins by arylamines.

References

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*The problem is to prevent the formation of acetanilide which is formed predominantly from the reaction of aniline with acetic acid, although acetanilide formed can be removed from the reaction mixtures by treating with concd. HCl.