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THE OXIDATION OF N,N-DIALKYLANILINES BY PALLADIUM(II) ACETATE

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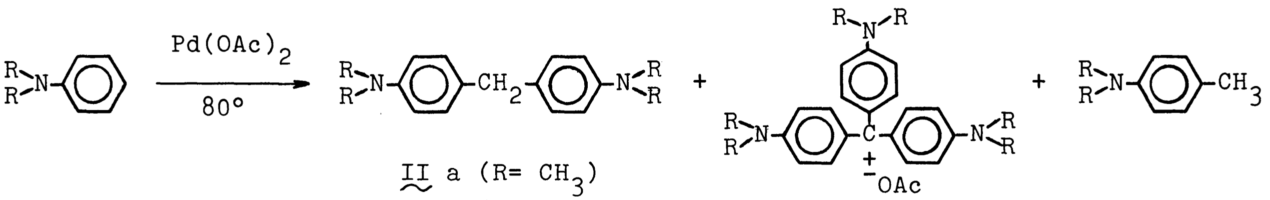
The reaction of N,N-dialkylanilines with palladium(II) acetate gave N,N,N',N'-tetraalkyldiaminodiphenylmethanes (II) as major products. The origin of -CH_2- in II seems to be the methyl group of palladium(II) acetate and the compound II may be derived from further oxidation of N,N-dialkyltoluidine primarily formed.

A wide variety of aromatic compounds are known to be oxidized by palladium(II) salts to give aromatic coupled products or functionalized aromatics,[1] e.g. the reaction of toluene or anisole with palladium(II) acetate gave biphenyl derivatives and aromatic acetates.[2] However, in a course of our studies on the reaction of aromatic compounds with palladium(II) salts,[3] we have found that N,N-dialkylanilines give quite different products.

In a typical experiment, N,N-dimethylaniline (2.4 g, 0.02 mole) was reacted with palladium(II) acetate (2.2 g, 0.01 mole) in acetic acid (60 g, 1.0 mole) at 80° for 5 hr under nitrogen atmosphere. Palladium(II) acetate was quantitatively reduced to metallic palladium and all of N,N-dimethylaniline was consumed. Organic products were separated by silica gel chromatography and identified by ir, nmr, uv, mass, glc, and elemental analysis. N,N,N',N'-Tetramethyldiaminodiphenylmethane (IIa) was isolated in a yield of 72.1% together with 16.3% of crystal violet (IIIa) and trace of N,N-dimethyl-p-toluidine (Ia). The yields of products are based on the reacted N,N-dimethylaniline. The results of similar reactions are summarized in Table 1.

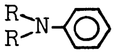


II a (R= CH_3)
b (R= C_2H_5)

III

I

Table 1. The Oxidation of N,N-Dialkylanilines with Palladium(II) Acetate

Reactant[a]	Solvent	Reaction time, hr	Products, %[b]		
			p-Toluidine (I)	Diarylmethane (II)	Crystal Violet (III)
R= $-CH_3$	Acetic acid	5	trace	72.1	16.3
$-CH_3$	Acetic acid	1	trace	76.3	18.6
$-CH_3$	Acetonitrile	5	trace	54.0	none[c]
$-CH_3$	Dioxane	5	2.2	55.7	none[d]
$-C_2H_5$	Acetic acid	5	trace	$\sim$5	small[e]

a. $Pd(OAc)_2$ (0.01 mole) and N,N-dialkylanilines (0.02 mole) were heated at 80° in the solvent described in Table 1 (1.0 mole) under nitrogen.

b. The yields are based on the reacted N,N-dialkylanilines.

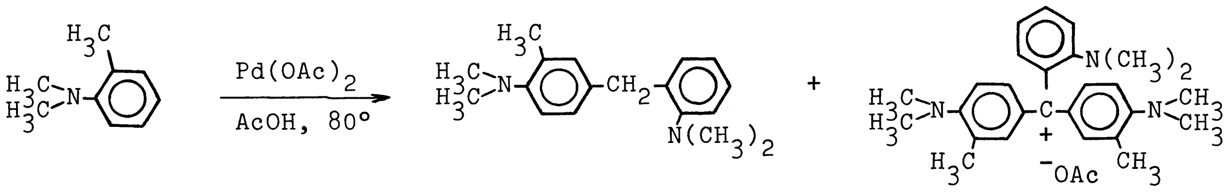
c. N,N,N',N'-Tetramethylbenzidine was isolated as other product in a yield of 14.7%.

d. N,N-dimethyl-p-aminobenzoic acid was isolated as other product in a yield of 21.5%.

e. Dealkylated products were mainly obtained, such as N-ethylaniline (18.6%), N-ethylacetanilide (8.2%), acetanilide (2.6%), and so on.

As shown in Table 1, the formation of diarylmethane (II) was observed in both protic and aprotic solvents in good yields. Especially in acetic acid, the total yield of IIa and IIIa was almost 90% or more and the N-methyl groups of N,N-dimethylaniline were retained in N-position of IIa and IIIa. Furthermore, N,N-diethylaniline also gave a corresponding diarylmethane (IIb). Therefore, the origin of $-CH_2-$ in II is considered to be methyl group of palladium(II) acetate, although the possibility cannot be completely eliminated that N-methyl carbon might be partly transformed to the methylene of II.[4]

The formation of N,N-dialkyl-p-toluidines (I) was observed in all reactions, though the yields of I were relatively low. In further experiments, the reaction of a mixture of N,N-dimethylaniline (0.05 mole) and N,N-dimethyl-p-toluidine (0.05 mole) with palladium(II) acetate (0.01 mole) in acetic acid (1.0 mole) at 80° gave 117% of IIa, along with trace of IIIa.[5] Moreover, the reaction of N,N-dimethyl-o-toluidine (0.02 mole) with palladium(II) acetate (0.01 mole) gave 11.0% of 3,2'-bis(N,N-dimethylamino)-4-methyldiphenylmethane (IV) and 21.0% of crystal violet (V, λ_{max}^{EtOH} 572 nm), showing that the methylated aromatics may gave diarylmethane by palladium(II) acetate under the present conditions.[6]



IV V

Consequently, the oxidation of N,N-dimethylaniline by palladium(II) acetate is considered to proceed via methylation of aromatic ring to form N,N-dimethyl-p-toluidine (I) as a primary product. The further reaction of I with N,N-dimethylaniline, in situ, produces N,N,N',N'-tetramethyldiaminodiphenylmethane (II), which may undergo further oxidation to give crystal violet (III).

The oxidation of N,N-dimethylaniline by one electron oxidant, e.g. peroxydisulfate ion ($S_2O_8^{2-}$) which is known to decompose thermally into sulfate radical anion ($SO_4^{\cdot -}$),[7] gave the same products described above. In our experiment, the reaction of N,N-dimethylaniline (0.02 mole) with sodium peroxydisulfate (0.01 mole) and sodium acetate (0.04 mole) in acetic acid (100 ml) at 100° for 4 hr gave 40.6% of IIa and a small amount of IIIa.[8] The similar results were also reported in the electrochemical oxidation of N,N-dimethylaniline in acetonitrile.[4,9] One of the reasonable intermediates in these reactions should be N,N-dimethylaniline radical cation.

The analogy in products suggests the formation of radical cation species in the present palladium-oxidation.

Further investigation on these reactions is now in progress.

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References and Notes

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2) J. Davidson and C. Triggs, Chem. & Ind. (London), 457 (1966).

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4) In the electrochemical oxidation of N,N-dimethylaniline, the origin of $-CH_2-$ in II has been expalined to be N-methyl group of N,N-dimethylaniline, and therefore the yields of II never exceed 50%; R. Hand and R. F. Nelson, J. Electrochem. Soc., 117, 1353 (1970).

5) The yields are based on the reacted N,N-dimethylaniline.

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7) A. Ledwith, P. J. Russel, and L. H. Sutcliffe, J. Chem. Soc. Perkin II, 630 (1973).

8) The formation of demethylated products, such as N-methylacetanilide (8.3%) and N-acetyl-N,N',N'-trimethyldiaminodiphenylmethane (3.5%), was observed.

9) The similar products also have been obtained in the reaction of N,N-dimethylaniline with benzoyl peroxide; J. M. Fayadh, D. W. Jessop, and G. A. Swan, Proc. Chem. Soc., 236 (1964); R. B. Roy and G. A. Swan, Chem. Commun., 427 (1966).

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