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Reaction of *N,N*-Dialkylanilines with Palladium(II) Compounds

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The reaction of *N,N*-dialkylaniline with palladium(II) acetate or di-μ-acetato-bis[α-(dimethylamino)-*o*-tolyl]-dipalladium (**B**) gave 4,4′-bis(dialkylamino)diphenylmethane as a major product. It was elucidated that the origin of $-CH_2-$ in the product might be methyl group of palladium acetate and the primary reaction product might be *N,N*-dialkyltoluidine. The absorption spectra of the initial reaction mixture of *N,N*-dimethylaniline with **B** in acetic acid at room temperature showed the absorption maximum at 470 nm and at 750 nm. The latter peak was tentatively assigned to *N,N*-dimethylaniline radical cation–palladium(I) acetate complex, which was suggested as a key-intermediate for the formation of diarylmethanes.

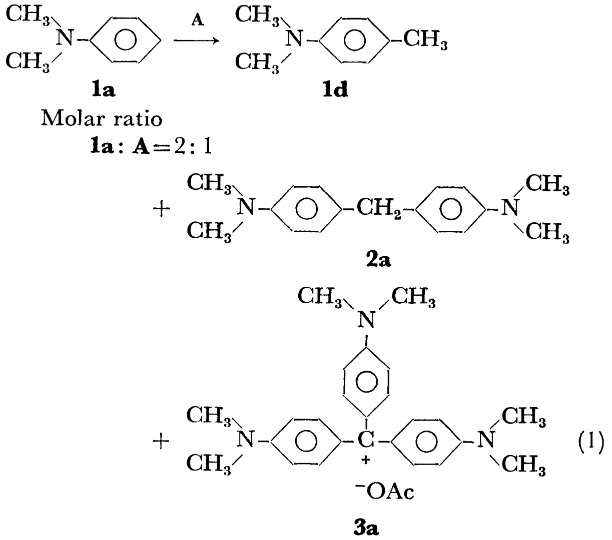
A large number of studies on the reactions of many aromatic compounds with palladium(II) salts have been actively done,[1] since van Helden and Verberg presented the oxidative coupling of aromatic rings with palladium(II) chloride.[2] In exploring the synthetic utility of palladium-assisted aromatic substitution, two types of investigation have been carried out. One is concerned with substitution of vinylic hydrogen by aryl groups,[3,4] and another is on the functionalization of aromatic rings by other nucleophiles.[5] In both studies, various monosubstituted aromatic compounds have been used as reactants. However, to our knowledge, no information on the reaction of aniline derivatives with palladium(II) salts have been presented so far.[6]

N,N-Dialkylanilines have relatively low ionization potential. For example, those of *N,N*-dimethylaniline and *N,N*-diethylaniline are 7.12 and 6.99 eV, respectively.[7] These values are much smaller than the ionization potentials of other aromatic compounds such as nitrobenzene (9.92 eV), methyl benzoate (9.35), benzene (9.24), chlorobenzene (9.07), toluene (8.82), anisole (8.21), and so on. Thus, we might expect some different reactivity of aniline derivatives for palladium(II) salts.

We have already communicated that *N,N*-dialkylanilines react with palladium(II) acetate to give diarylmethanes as a major product.[8] The reaction was quite different from generally known aromatic oxidative coupling or aromatic functionalization with palladium(II) salts. The reaction involves some novel reaction paths such as aromatic methylation and benzylic arylation.[9] Therefore, further investigation was carried out on the reactions of *N,N*-dimethylanilines with some palladium(II) compounds. In this report, the detailed information and the spectroscopic data will be presented and some reaction intermediates will be also suggested.

Results and Discussion

N,N-Dimethylaniline (**1a**) reacted with a half equimolecular palladium(II) acetate (**A**) in acetic acid at 80 °C to give *p*-toluidine (**1d**) (trace), 4,4′-bis(dimethylamino)diphenylmethane (**2a**) (72.1%), and Crystal Violet (**3a**) (16.8%). **A** was quantitatively reduced to metallic palladium and all of **1a** was consumed. However, no *N,N,N′,N′*-tetramethylbenzidine was detected on GLC of the organic product mixture. Although a mixture of **1a** (0.02 mol) and acetic acid (1.0 mol) was heated in the absence of **A** at 80 °C for 5 h under nitrogen atmosphere, none of **2a** was obtained and 96% of the used **1a** was recovered. The results of reactions of *N,N*-dialkylanilines with **A** are summarized in Table 1.



In acetonitrile or dioxane, the reaction of **1a** with **A** proceeded similarly to that in acetic acid to give diarylmethane (**2a**) as a major product. However, it can be seen in Table 1 that the reaction in aprotic solvent is relatively slower than in acetic acid. Furthermore, the yield of some by-products such as *N,N,N′,N′*-terametylbenzidine (**6**) or dimethylaminobenzoic acid (**7**) somewhat increased in aprotic solvents (14.7% and 2.15%, respectively).

These results clearly show that formation of diarylmethane is the major path in the reaction of *N,N*-dialkylanilines with palladium(II) acetate (**A**), and that the charactor of solvents has some influence on the reaction sequences.

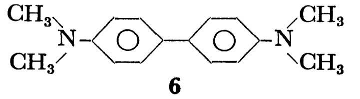
The conversion of **1a** to **2a** has been reported in the electrochemical oxidation at high concentration of **1a** in acetonitrile,[10] in which the origin of $-CH_2-$ in **2a** has been explained to be *N*-methyl group of **1a**, since the yields of **2a** never exceeded 50%.

In the present reaction, the yield of **2a** was usually higher than 50% (Table 1). Moreover, the reaction of **1b** with **A** gave **2b**, although in relatively low yield due to the accompanied dealkylation.[8] These facts suggest that the origin of $-CH_2-$ group in **2a** is not the

Table 1. The reaction of *N*,*N*-dialkylanilines with **A**

Reactant[a)]	Sovlent	Reaction time/h	Conversion[b)] of **1**/%	Products, (yield/%)[c)]
1a	Acetic acid	5	100	**1d** (trace), **2a** (72.1), **3a** (16.3)
1a	Acetic acid	1	75	**1d** (trace), **2a** (76.3), **3a** (18.6)
1a	Acetonitrile	5	46	**1d** (trace), **2a** (54.0), **6** (14.7)
1a	Dioxane	5	17	**1d** (2.2), **2a** (55.7), **7** (21.5)
1b	Acetic acid	5	40	**1e** (trace), **2b** (≈5), **3b** (small)
1c	Acetic acid	5	70	**2c** (11.0), **3c** (21.0)
1d	Acetic acid	5	69	**2d** (8.2), **4** (2.7)

a) **A** (0.01 mol) and **1** (0.02 mol) were heated in the solvent (1.0 mol) at 80 °C under nitrogen atmosphere. b) Calculated from the unreacted **1**. c) The yields are based on the reacted **1**.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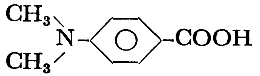
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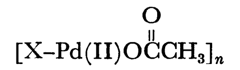
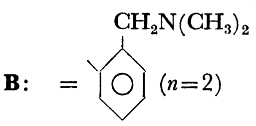
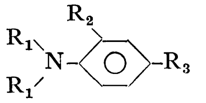
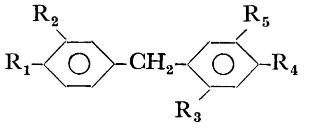

$[\text{X-Pd(II)O}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_3]_n$

A: $X=OCOCH_3$ $(n=1)$

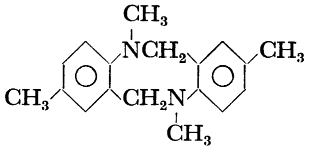

B: $(n=2)$



1a: $R_1=CH_3$, $R_2=R_3=H$
b: $R_1=C_2H_5$, $R_2=R_3=H$
c: $R_1=R_2=CH_3$, $R_3=H$
d: $R_1=R_3=CH_3$, $R_2=H$
e: $R_1=C_2H_5$, $R_2=H$, $R_3=CH_3$



2a: $R_1=R_4=\text{-N(CH}_3)_2$, $R_2=R_3=R_5=H$
b: $R_1=R_4=\text{-N(C}_2H_5)_2$, $R_2=R_3=R_5=H$
c: $R_1=\text{-N(CH}_3)_2$, $R_3=\text{-NH(CH}_3)$, $R_2=CH_3$, $R_4=R_5=H$
d: $R_1=R_3=\text{-N(CH}_3)_2$, $R_2=R_4=H$, $R_5=CH_3$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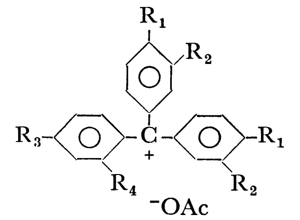
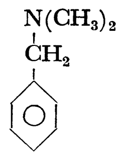


3a: $R_1=R_3=\text{-N(CH}_3)_2$, $R_2=R_4=H$
b: $R_1=R_3=\text{-N(C}_2H_5)_2$, $R_2=R_4=H$
c: $R_1=R_4=\text{-N(CH}_3)_2$, $R_2=CH_3$, $R_3=H$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N-methyl group of the reactant (**1a**), but methyl group of palladium(II) acetate (**A**). As the formation of **1d** or **1e** was always observed in the reactions of **1a** or **1b**, the aromatic methylation by **A**, followed by further arylation of the product (**1d** or **1e**), might occur to give **2a** or **2b**. Thus, the reaction of a mixture of **1a** and **1d** with **A** was carried out, in order to know the possibility of the further arylation of **1d**. Namely, a 1: 1 mixture of **1a** and **1d** in acetic acid was heated in the presence of **A** at 80 °C for 5 h, and the yields of produced diarylmethane (**2a**) were calculated according to both Eqs. 2 and 3 as in Table 2. The yields of **2a** were higher than quantitative yield based on Eq. 1, which meant that Eq. 2 is at least partly operative. Thus, **1d** should be one of reactants for the formation of **2a**.

$$2\,\mathbf{1a} \xrightarrow{\text{A}} \mathbf{2a} \qquad (2)$$

$$\mathbf{1a} + \mathbf{1d} \xrightarrow{\text{A}} \mathbf{2a} \qquad (3)$$

Further supporting evidences for benzylic arylation are that the reaction of **1d** with **A** in acetic acid gave diarylmethane (**2d**), along with cyclic dimer (**4**) and that **1c** yielded **2c** together with **3c** (Table 1).

Consequently, it is likely that the first product in the reaction of *N*,*N*-dialkylaniline (**1a** or **1b**) with **A** should be *N*,*N*-dialkyltoluidine (**1d** or **1e**). **1d** or **1e** might be furthermore oxidized by **A** to give diarylmethane (**2a** or **2b**), followed by reoxidation into Crystal Violet (**3a** or **3b**). However, another problem remains since the stoichiometry of **1a** shows that a formation of 1 mol of **2a** from **1a** should result in a reduction of 1 mol of **A** to metallic palladium (Table 1). The successive oxidation mechanism might possibly consume 2 mol of **A** for a formation of 1 mol of **2a**.

Di-*μ*-acetato-bis[α-(dimethylamino)-*o*-tolyl]dipalladium (**B**) can also oxidize **1a** in acetic acid under mild conditions. Even at room temperature, **B** was gradually decomposed to give diarylmethane (**2a**). The results of reactions in various conditions at 80 °C are summarized in Table 3. It clearly elucidates that the reaction of **1a** with **B** undergoes remarkably large effect of proton on the reaction rate. Namely, in aprotic solvents such as *N*,*N*-dimethylaniline, dioxane, or tetrahydrofuran the reaction never went on even at 96 °C. However, in the presence of proton, the oxida-

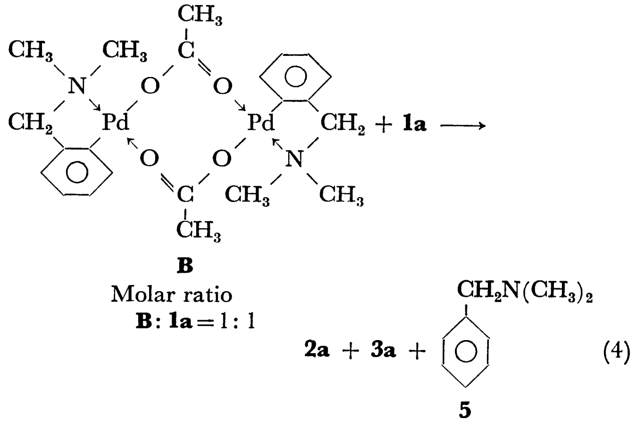


Table 2. Oxidation of mixed **1a** and **1d** with **A**

Reactants/mol[a]	Yield of **2a**[b]/%	
	Based on Eq. 2	Based on Eq. 3
1a (0.01), **1d** (0.01)	109.8	54.9
1a (0.02), **1d** (0.02)	99.3	49.4
1a (0.05), **1d** (0.05)	116.6	58.3

a) The reaction of the reactants with **A** (0.02 mol) in acetic acid (1.0 mol) was carried out at 80 °C under nitrogen atmosphere. b) The yields are based on the reacted **1a**.

tion completely proceeded to give **2a** in good yields. The poor yield of **3a** might possibly be expalined by steric hindrance in the contact between **2a** and palladium complex by benzylamine ligand. Therefore, the result suggests that the oxidation of **1a** with **B** may proceed *via* similar reaction sequences to the case of **A**.

The UV spectrum of **1a** in acetic acid shows a long-wavelength absorption maximum at 290 nm (ε 2.0 × 10^2), while palladium complex (**B**) has it at 330 nm (ε 1.0 × 10^3) (Fig. 1). These compounds have no absorption maximum in the longer wave region.

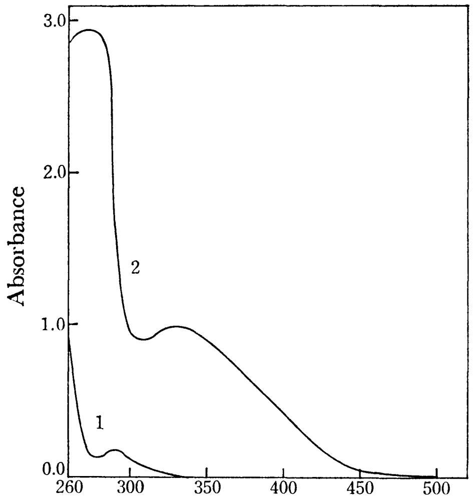


Fig. 1. Absorption spectra of **1a** (1) and **B** (2).
The spectra were measured in 1.0 × 10^{-3} M acetic acid solution at room temperature. (1 M = 1 mol dm^{-3}).

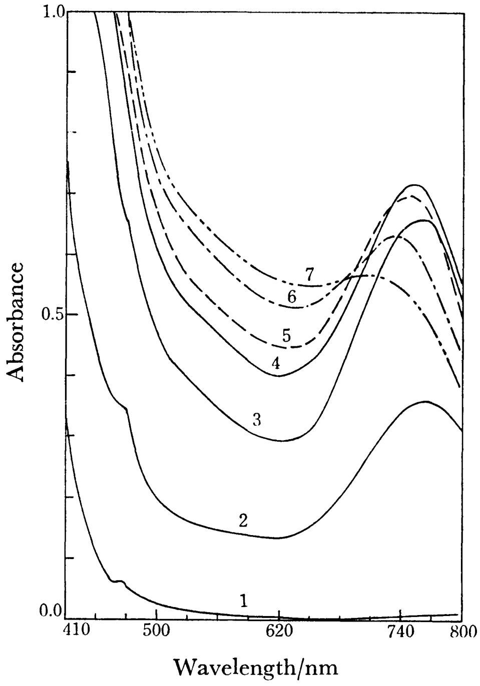


Fig. 2. Spectral change of reaction mixture of **1a** and **B** in acetic acid at room temperature under nitrogen atmosphere. Reaction time (min); 1: 0.5, 2: 10, 3: 30, 4: 50, 5: 60, 6: 80 7: 100.

However, when **B** and **1a** were mixed at room temperature (23 °C) in acetic acid under nitrogen atmosphere, a new absorption appeared at 470 nm, which could not be observed after about 50 min due to strong absorption enhancement in shorter wave region. Furthermore, another strong peak in a visible region appeared about 10 min after mixing. The visible spectra of a mixture of **1a** and **B** in acetic acid are shown in Fig. 2. The spectra indicate a clear appearance of new absorption maximum at 750 nm. Figure 3 shows the time dependent change of the 750 nm peak. The absorption had maximum in 48 min under measurement conditions and afterwards gradually decayed.

The peak at 470 nm appears immediately after mixing of **1a** and **B**, and its intensity looks relatively weak. Therefore, the formation rate of the intermediate related with 470 nm peak might be relatively rapid.

Table 3. The solvent effect on the reaction of **1a** with **B**[a]

Solvents	Reaction temp/°C	Recovered **B**/%	Product yields/%		
			2a[a]	**3a**[b]	**5**[c]
Acetic acid (1.0)	80	8	43	3	60
Acetic acid (0.5) and **1a** (0.5)	80	0	99	0	84
1a (1.0)	80	100	0	0	0
1a (1.0), HCl(0.06)[d]	80	0	81	0	75
Tetrahydrofuran (1.0)	65	100	0	0	0
Dioxane (1.0)	80	100	0	0	0
Dioxane (1.0)	96	98	0	0	0

a) **B** (0.01 mol as the dimeric form) and **1a** (0.04 mol) were used, if not indicated in the table. b) Isolated yields based on the reacted **1a**. c) Yields based on the reacted **B**. They were determined by NMR analyses of reaction mixture. d) 5 ml of 12 M HCl was used.

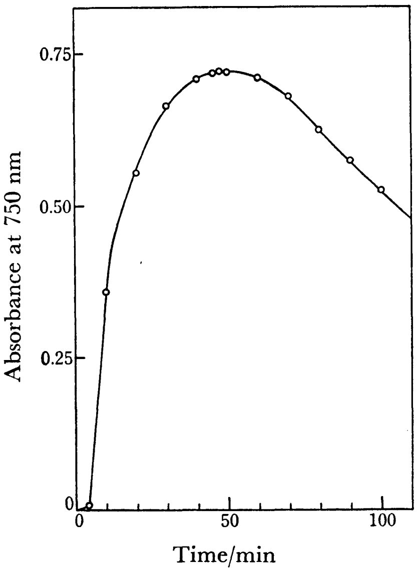
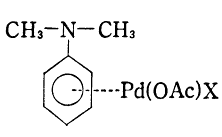
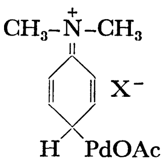


Fig. 3. Time dependence of the absorbance at 750 nm.

The well-known primary intermediates in the reaction of aromatic compounds with palladium(II) salt are π- or σ-complexes between aromatics and palladium, which are readily formed in a rapid process.[2] Thus, the origin of 470 nm peak might be tentatively assigned to the complex $\mathbf{C}_1$ or $\mathbf{C}_2$. However, another possibility can not be completely eliminated that the absorption at 470 nm[12] might be concerned with a radical cation intermediate, in relation to the assignment of 750 nm peak.



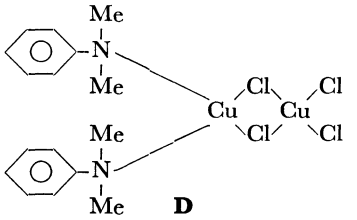
$\mathbf{C}_1$

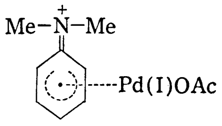


$\mathbf{C}_2$

The second peak at 750 nm has appeared after some induction period and has some life time. It is noteworthy that the absorption was in a remarkably long wave region and the intensity was considerably strong. The analogous peak has also been observed in the reaction of **1a** under different conditions; first, electrochemical study of **1a** in acetic acid showed the absorption peaks at 469 nm and at 750 nm, which were assigned to oxidized *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMBOx) and 2: 1 **1a**: TMBOx adduct, respectively.[15] Second, the oxidation of **1a** with copper(II) chloride in ethanol showed λ_{max} at 472 nm and 740 nm, in which the latter peak was assigned to the 1: 1 **1a**: copper(II) chloride complex (**D**).[16]

In the present reaction in acetic acid, *N*,*N*,*N*′,*N*′-tetramethylbenzidine (**6**) was never a product. It is also unlikely that a similar palladium(II) complex to **D** may have such a long-wavelength absorption. Therefore, we would suggest the formation of a radical cation–palladium(I) complex (**E**) and tentatively assign the peak at 750 nm to the complex (**E**).[17]



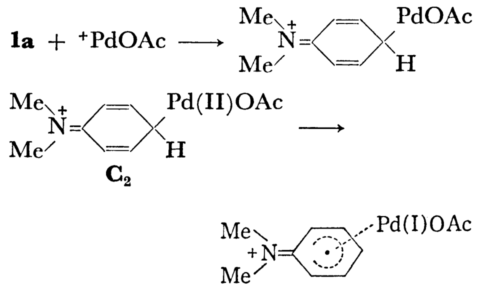


E

The radical cation complex (**E**) could be formed *via* σ-complex ($\mathbf{C}_2$) because of a low ionization potential of *N*,*N*-dialkylaniline (Eqs. 5, 6, and 7).

$$\text{X–Pd–OAc} + \text{H}^+ \longrightarrow {}^+\text{PdOAc} + \text{HX} \qquad (5)$$

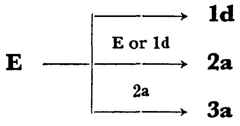
A or **B**



(6)

(7)

In conclusion, the complex (**E**) is suggested to be a key-intermediate to the products (**1d**, **2a**, and **3a**).



Experimental

Materials. Palladium(II) acetate (**A**) and di-μ-acetato-bis[α-(dimethylamino)-*o*-tolyl]dipalladium (**B**) were prepared according to the methods of Stephenson *et al.*[18] and R. Heck *et al.*,[19] respectively. Commercially available *N*,*N*-dialkylanilines were used after distillation under a reduced pressure and drying on anhydrous sodium sulfate before use.

TABLE 4. ^{1}H NMR DATA OF ISOLATED PRODUCTS

Compound	τ-Value			
	N-CH$_3$ (or C$_2$H$_5$)	Other-CH$_3$	-CH$_2$-	Aroma-H
2a	7.06 (s, 12H)		6.11 (s, 2H)	2.94 (q, 8H)
2b	8.90 (t, 12H), 6.70 (q, 8H)		6.23 (s, 2H)	3.04 (q, 8H)
2c	7.33 (s, 6H), 7.14 (s, 3H)	7.93 (s, 3H)	6.02 (s, 2H)	2.73—3.60 (m, 7H)
2d	6.01 (s, 6H), 7.49, 7.13 (s, 3H, resp.)	7.66 (s, 3H)	6.08 (s, 2H)	2.47—3.29 (m, 7H)
3a	6.90—7.40 (m, 18H)	8.74 (s, 3H)		2.43—3.32 (m, 12H)
4	7.19 (s, 6H)	7.70 (s, 6H)	5.80 (s, 4H)	2.66—3.20 (m, 6H)

a) Measured in CDCl$_3$ using TMS as internal standard.

Measurements. UV and visible spectra were measured by Shimadzu multipurpose MPS-50L spectrophotometer. IR and PMR measurements were carried out by JASCO IRA-I and JEOL JNM60 apparatus, respectively. The NMR data of obtained products are summarized in Table 4.

The spectral change of the reaction of **1a** with **B** was recorded at an appropriate time after adding 15.18 mg of **1a** to 25 ml of 1.0×10^{-3} M acetic acid solution of **B** under nitrogen atmosphere at room temperature (23 °C). The scan time (410—800 nm) was 1.5 min.

Reaction of N,N-*Dimethylaniline (1a) with Palladium(II) Acetate (A).* A stirred mixture of **1a** (2.4 g, 0.02 mol) and **A** (2.2 g, 0.01 mol) in acetic acid (60 g, 1.0 mol) was heated at 80 °C for 5 h under nitrogen atmosphere. A filtration of the reaction mixture gave metallic palladium (1.1 g, 0.01 mol). The filtrate was evaporated to remove the solvent. It was confirmed by TLC and GLC of the evaporated residue that all of used **1a** was consumed and that trace of *N,N*-dimethyl-*p*-toluidine (**1d**) was obtained. The residue was column-chromatographed using 90 g of Wacogel. The elution by benzene gave 1.83 g of 4,4′-bis(dimethylamino)diphenylmethane (**2a**) (72.1%), which was recrystallized from benzene–petroleum ether: plates, mp 86.5—87.0 °C (lit,[16] mp 89.5—90.5 °C), UV; $\lambda_{\max}^{\mathrm{EtOH}}$ 261.8 nm (ε 3.04×10^4), Mass (*m/e*); 254 (M^+-Me_2), 134. The elementary analyses for C, H, and N were correctly analyzed. Further elution by a mixed solvent of ethyl ether and ethanol gave 0.483 g of Crystal Violet (acetate salt) (**3a**): UV; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 596.2 nm (lit, as chloride salt,[20] 590 nm), IR (KBr disk, in cm^{-1}); 1660—1550 (br, aromatic C=C and CH_3COO^-). The reactions of *N,N*-dialkylaniline with **A** or **B** in various solvents were similarly treated as described above. The yields of **2a** in the reactions of **1a** and **1d** mixture with **A** were determined by GLC analysis using SE 30 on chromosorb (270 °C, carrier gas H_2) and using the identified **2a** sample as an authentic material. **6** and **7** were identical with their specimen on IR and NMR spectra and GLC.

Reaction of N,N-*Dimethyl*-p-*toluidine (1d) with A.* A stirred mixture of **1d** (2.7 g, 0.02 mol) and **A** (2.2 g, 0.01 mol) in acetic acid (60 g, 1.0 mol) was heated at 80 °C for 5 h under nitrogen atmosphere. The filtration of the reaction mixture gave metallic palladium (1.1 g, 0.01 mol). The filtrate was distilled under a reduced pressure to remove the solvent and the unreacted toluidine. The distillate contained 0.84 g of unreacted **1d**, from the result of GLC analysis. The distilled residue was column-chromatographically separated using 300 g of Wacogel. The elution by a mixed solvent of petroleum ether (50%) and chloroform (50%) gave 44 mg of the solid which was recrystallized from dichloromethane. It was identified with dibenzodiazocine derivative (**4**) from following data: mp 147.0—147.5 °C, Mass (*m/e*); 266 (M^+), 254 (M^+-CH_3), 146, 134.

Found: C; 81.27, H; 8.39, N; 10.39%. Calcd for $C_{18}H_{22}N_2$: C; 81.20. H; 8.27, N; 10.53%. The NMR data are shown in Table 3. Further elution by petroleum ether (30%) and chloroform (70%) gave 86 mg of diarylmethane (**2d**) (8.2%), followed by 86 mg of *N, p*-dimethylacetoanilide (3.8%) which were identified with authentic materials by GLC, IR, and NMR.

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References

1) P. Maitlis, "The Organic Chemistry of Palladium," Academic Press, New York and London (1971), Vol. II, pp. 60—71.

2) R. van Helden and G. Verberg, *Rec. Trav. Chim. Pays-Bas*, **84**, 1263 (1965).

3) a) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Am. Chem. Soc.*, **91**, 7166 (1969); therein cited references; b) R. S. Shue, *Chem. Commun.*, **1971** 1510.

4) R. F. Heck, *J. Am. Chem. Soc.*, **91**, 6707 (1969).

5) a) P. Henry, *Tetrahedron Lett.*, **1968**, 2285; *J. Org. Chem.*, **36**, 1886 (1971); b) T. Tisue and W. Downs, *Chem. Commun.*, **1969**, 410; c) L. Eberson and L. Gomez-Gonzales, *ibid.*, **1971**, 263; d) H. Yoshimoto and H. Itatani, *Bull. Chem. Soc. Jpn.*, **46**, 2490 (1973); e) R. Normann, W. Parr, and C. Thomas, *J. Chem. Soc.*, *Perkin Trans. 1*, **1974**, 369; f) T. Sakakibara and Y. Odaira, *J. Org. Chem.*, **41**, 2049 (1976).

6) Recent communication showed that the reaction of styrene with arylamines by **A** gave stilbene derivatives *via* C–N bond cleavage of arylamines; F. Akiyama, S. Teranishi, Y. Fujiwara, and H. Taniguchi, *J. Organomet. Chem.*, **140**, C7 (1977).

7) J. L. Franklin, J. D. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Handbook of Chemistry and Physics," 50th ed, ed by R. C. Weast, the Chemical Rubber Co., (1969), pp. E80—E86.

8) T. Sakakibara, J. Kotobuki, and Y. Dogomori, *Chem. Lett.*, **1977**, 25.

9) The formation of diarylmethanes from *p*-xylene by **A** in trifluoroacetic acid has been reported; F. R. S. Clark, R. O. C. Norman, C. B. Thomas, and J. S. Willson, *J. Chem. Soc.*, *Perkin Trans. 1*, **1974**, 1289.

10) R. Hand and R. F. Nelson, *J. Electrochem. Soc.*, **117**, 1353 (1970).

11) J. Davidson and C. Triggs, *Chem. Ind. (London)*, **1966**, 457.

12) UV iradiation of **1a** in rigid matrices at 77 K has been investigated by some workers.[13] They observed the primary absorption peak near 460—470 nm region and assigned it to the *N,N*-dimethylaniline radical cation. But recently, some doubt has been cast on these data,[14] since spectroscopic studies on electrochemically oxidized *N,N,N′,N′*-tetramethylbenzidine (**6**) gained quite the same spectra.

13) a) G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.*, **65**, 2419 (1943); b) G. Porter and F. Wright, *Trans. Faraday Soc.*, **51**, 1469 (1955); *ibid.*, **54**, 2027 (1958); c) S. Arimitsu, K. Kimura, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **42**, 1858 (1969).

14) a) N. L. Weinberg, "Technique of Electroorganic Synthesis," John Wiley and Sons, Inc., (1974), Part I, pp. 652—653; b) R. F. Nelson, Ph. D. Thesis, Kansas University (1966).

15) a) Ref. 14a, p. 656; b) J.-E. Dubois, P.-C. Lacaze, and A. Aranada, *C. R. Acad. Sci., Paris*, **260**, 3383 (1965).

16) J. R. L. Smith, R. O. C. Norman, and W. M. Walker, *J. Chem. Soc., B*, **1968**, 269.

17) A magneta complex of palladium(I) containing benzene has been isolated. The complex showed absorption maximum at 380 nm and 550 nm in acetic acid; J. M. Davidson and C. Triggs, *J. Chem. Soc., A*, **1968**, 1324.

18) T. Stephenson, S. Morehouse, A. Powell, J. Heffer, and G. Willkinson, *J. Chem. Soc.*, **1965**, 3632.

19) J. M. Thomson and R. F. Heck, *J. Org. Chem.*, **40**, 2667 (1975).

20) H. Sato, *Bull. Chem. Soc. Jpn.*, **38**, 1719 (1965).