Supporting Information

Understanding Reactivity Patterns of Dialkylaniline Radical Cation

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1. General experimental techniques

Absorption spectra were recorded on a Diode Array Spectrophotometer. ^1H NMR spectra were obtained on a 300 MHz Spectrometer. Purity of all products were tested by GC-MS. IR spectra were recorded on a FTIR Spectrometer. All solvents and commercially available chemicals were used without additional purification. All experiments were carried out at room temperature (25 ± 1 °C), unless otherwise mentioned.

2. Reactions

(a) Reaction of DMA with Cu^{2+} : Preparation of *N,N,N',N'*-Tetramethylbenzidine (TMB)

A solution of copper (II) perchlorate hexahydrate (5.5 g, 15 mmol) in CH_3CN (10 mL) was added to a solution of *N,N*-dimethylaniline (1.2 g, 10 mmol) in CH_3CN (10 mL) over a period of 30 min at 25 °C and the mixture stirred for 10 h. Solid K_2CO_3 (4.0 g) was added and stirring continued for 0.5 h. Filtered and the solids were washed twice with CHCl_3 . The combined organic extract was washed with water and dried over anhydrous Na_2SO_4 . GC-MS of the crude extract is given below.

The peak at retention time (RT) 22.111 is due to TMB. The minor peak ($\approx 10\%$) at RT 19.07 also had the same molecular mass and is assigned to a *ortho, para* coupled product (no attempt was made to isolate this product). The solvent was removed and the residue so obtained was recrystallized from petroleum ether. GC-MS of recrystallized product is given below. Yield of pure product was 1.0 g (83 %), mp. 195-196 °C. (reported mp 195 °C). ^1H NMR (CDCl_3 , 300 MHz) δ : 7.4 (d, 4 H), 6.7 (d, 4 H), 2.9 (s, 12 H).

(b) *Reaction of DEA with Cu^{2+}* : The reaction was carried out in the same way to yield tetraethylbenzidine. Yield 86%, mp. 85 °C. (reported mp 85 °C).² ^1H NMR (CDCl_3 , 300 MHz) δ : 7.4 (d, 4 H), 6.7 (d, 4 H), 3.4 (q, 8 H), 1.2 (t, 12 H).

(c) *Reaction of DMA^{++} with Chloride ions: Preparation of 4-Chloro-*N,N*-dimethylaniline:*

A solution of *N,N*-dimethylaniline (121 mg, 1 mmol) in acetonitrile (10 mL) was added to a solution of copper (II) chloride dihydrate (340 mg, 2 mmol) in acetonitrile (30 mL) and the mixture stirred for 10 h at room temperature. Solid K_2CO_3 (1.0 g) was added and stirring continued for 10 minutes. The reaction mixture was filtered and the solids were washed twice with CHCl_3 . The combined organic extract was dried over anhydrous Na_2SO_4 . GCMS of the crude extract is shown below.

The peak at RT 10.71 is due to 4-chloro-*N,N*-dimethylaniline. The peak at RT 22.10 is due to TMB.

The solvent was removed and the residue was chromatographed on alumina column. Elution with petroleum ether gave pure 4-chloro-*N,N*-dimethylaniline (80 mg, 52 %). mp. 33-34 °C (reported mp 35 °C).³ ^1H NMR (CDCl_3 , 300 MHz) δ : 7.0 (d, 2 H), 6.5 (d, 2 H), 2.8 (s, 6 H). ^1H NMR Spectrum is shown below.

(d) *Reaction of DEA^{++} with Chloride ions:* The reaction was carried out in the same manner to give 4-chloro-*N,N*-diethylaniline. Yield 58%, ^1H NMR (CDCl_3 , 300 MHz) δ : 7.0 (d, 2 H), 6.5 (d, 2 H), 3.4 (q, 4 H), 1.2 (t, 6 H).

(e) *Reaction of DMA^{++} with Bromide ions: Preparation of 4-Bromo-*N,N*-dimethylaniline:*

N,N-Dimethylaniline (121 mg, 1 mmol) and tetrabutylammonium bromide (640 mg, 2 mmol) were dissolved in CH_3CN (30 mL). A solution of copper (II) perchlorate hexahydrate (740 mg, 2 mmol) in CH_3CN (10 mL) was added and the mixture stirred for 0.5 h at room temperature. Solid K_2CO_3 (1.0 g) was added and stirring continued for 10 minutes. The reaction mixture was filtered and the solids were washed twice with CHCl_3 . The organic fractions were combined and dried over anhydrous Na_2SO_4 . GCMS of the crude extract is shown below. Only one peak was seen in the GCMS at RT 8.031 and this is due to 4-bromo-*N,N*-dimethylaniline.

The solvent was removed and the residue was taken in petroleum ether. This was filtered through a small alumina column and crystallized from the same solvent. Yield of pure product was 172 mg (86%), mp. 54-55 °C (reported mp 55 °C).⁴ ^1H NMR (CDCl_3 , 300 MHz) δ : 7.2 (d, 2 H), 6.5 (d, 2 H), 2.9 (s, 6 H). The ^1H NMR spectrum is shown below.

(f) *Reaction of DEA^{++} with Bromide ions*: The reaction was carried out in the same way to give 4-bromo-N,N-diethylaniline. Yield 88%, ^1H NMR (CDCl_3 , 300 MHz) δ : 7.2 (d, 2 H), 6.5 (d, 2 H), 3.4 (q, 4 H), 1.2 (t, 6 H).

(g) *Reaction of DMA^{++} with Thiocyanate: Preparation of 4-Thiocyanato-N,N-dimethylaniline*:

N,N-dimethylaniline (121 mg, 1 mmol) and sodium thiocyanate (160 mg, 2 mmol) were dissolved in CH₃CN (30 mL). A solution of copper (II) perchlorate hexahydrate (740 mg, 2 mmol) in CH₃CN (10 mL) was added and the mixture stirred for 0.5 h at room temperature. Solid K₂CO₃ (1.0 g) was added and stirring continued for 10 minutes. The reaction mixture was filtered and the solids were washed twice with CHCl₃. Organic extracts were combined and dried over anhydrous Na₂SO₄. GCMS of the crude extract is shown below.

The peak at RT 11.807 is due to 4-thiocyanato-*N,N*-dimethylaniline. There is a small peak at RT 18.225 and this is not identified.

The solvent was removed and the residue was taken in a mixture (9:1) of petroleum ether and chloroform and filtered through a small alumina column and crystallized from the same solvent mixture. Yield of pure product was 150 mg (84%), mp 73-74 °C. (reported 73-74 °C).⁵ IR (KBr): 2953, 2920, 2860, 2142, 1589, 1512, 1371, 1232, 1082, 968, 949, 808 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz) δ: 7.3 (d, 2 H), 6.5 (d, 2 H), 2.9 (s, 6 H). ¹H NMR spectrum is shown below.

(h) *Reaction of DEA⁺ with Thiocyanate*: The reaction was carried out in the same way to yield 4-thiocyanato-N,N-diethylaniline. Yield 85%, ¹H NMR (CDCl₃, 300 MHz) δ: 7.3 (d, 2 H), 6.6 (d, 2 H), 3.4 (q, 4 H), 1.2 (t, 6 H).

(3) References

1. Michler, W.; Pattinson, S. *Ber.* **1881**, 14, 2161.
2. Michler, W.; Pattinson, S. *Ber.* **1881**, 14, 2161.
3. Heidelberg, *Ber.*, **1887**, 20, 150.
4. Wurster, Beran, *Ber.*, **1879**, 12, 1820.
5. Khazaei, A.; Alizadeh, A.; Vaghei, R. G. *Molecules* **2001**, 6, 253.