Syntheses and Redox Properties of Di-, Tri-, Tetra-, and Pentaamines

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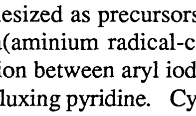
A series of di-, tri-, tetra-, and pentaamines were synthesized as precursors for corresponding di-, tri-, tetra-, and penta(aminium radical-cations) by the aryl-N bond formation reaction between aryl iodides and *in situ* prepared copper amide in refluxing pyridine. Cyclic voltammograms of *meta*-connected derivatives consisted of irreversible waves which imply side reactions in addition to oxidation to aminium radical-cations.

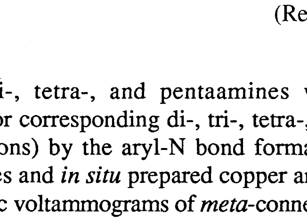
Poly(triarylamines) where nitrogen atoms are located at 1, 3- or 1, 3, 5- positions of aromatic rings are molecules of current interest because oxidation of them would afford high spin poly(triarylaminium radical-cations) if spins align ferromagnetically according to topological symmetry of π-conjugated systems and spin polarization.[1] Although there have been several reports on syntheses and oxidation of poly(*m*-anilines)[2] and tris(aminium radical-cation) is reported to be a quartet molecule,[3a, 3b] few systematic studies on a series of oligo(aminium radical-cations) to disclose and predict properties of poly(aminium radical-cations) have been carried out until now. We report here syntheses and redox properties of di- (**2a**, **2b**, **2c**), tri- (**3a**, **3b**), tetra- (**4**), and pentaamines (**5**).

Ar_3N

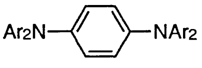
1a: Ar = 4-*t*-butylphenyl
1b: Ar = 4-anisyl



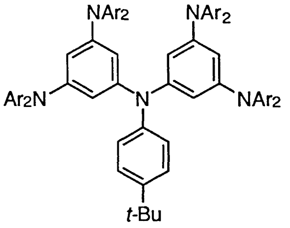
2a: Ar = 4-*t*-butylphenyl
2b: Ar = 4-anisyl

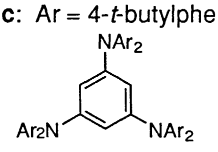


4: Ar = 4-*t*-butylphenyl



2c: Ar = 4-*t*-butylphenyl





3a: Ar = 4-*t*-butylphenyl
3b: Ar = 4-anisyl

5: Ar = 4-*t*-butylphenyl

Most of compounds which consist of several triarylamines known so far have been synthesized by Ullmann coupling,[4] *i. e.*, copper catalyzed coupling between aryl iodides and arylamines at high temperature (*ca.* 200 °C). For a systematic synthesis of oligoamines such as **5**, we needed an efficient method for N-C bond formation as a key step. After several attempts, reaction of copper amides and aryl halides for preparation of anilines by King and Walton[5] was successfully applied to the synthesis of these amines.

At first, di- (**2a**, **2b**, **2c**), tri- (**3a**, **3b**), and tetraamines (**4**) were synthesized by the coupling between aryl iodides and *in situ* prepared copper amide (eq. 1). For example, the diamine **2a** was synthesized as follows: Bis(4-*t*-butylphenyl)amine **6a** (282 mg, 1.00 mmol) in THF (10 ml) under Ar atmosphere was lithiated with butyllithium (1.62 mmol, 1.62 M in hexane) at 0 °C. After stirring at 0 °C for 1 h, the yellow solution was added to the white suspension of CuI[6] (316 mg, 1.66 mmol) in THF (3 ml) at 0 °C and the resulting black mixture was stirred at 0 °C for 30 min. To the mixture, 3,5-diiodo-*t*-butylbenzene (188 mg, 0.486 mmol) in pyridine (20 ml) was added at 0 °C. The mixture was refluxed for 12 h. After evaporating solvents under reduced pressure, the yellow solid was purified by column chromatography on SiO_2 (eluent: hexane, followed with hexane/CH_2Cl_2 = 10/1, CH_2Cl_2) to give **2a** (73%). Reaction of di-, tri-, and tetraiodides gave the corresponding amines and results are summarized in Table 1. The structure of products were confirmed by ^1H and ^{13}C NMR, mass spectra, and elemental analyses.

$$Ar_2NH \xrightarrow[\text{ii) CuI}]{\text{i) BuLi}} \xrightarrow[\text{pyridine, reflux}]{Ar'I} Ar_2Ar'N \quad \text{(eq. 1)}$$

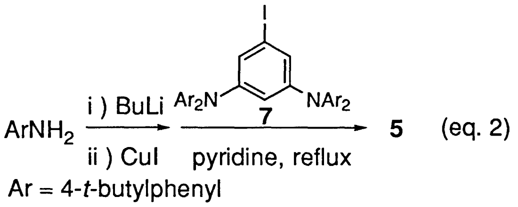
6a: Ar = 4-*t*-butylphenyl
6b: Ar = 4-anisyl

Table 1. The coupling between aryl iodide and copper amide

Run	Amine (mmol)	Aryl iodide (mmol)	Product (Yield/%[a])
1	**6a** (1.10)	4-iodo-*t*-butylbenzene (1.10)	**1a** (77)
2	**6a** (1.50)	1,4-diiodobenzene (0.50)	**2c** (40)
3	**6a** (1.00)	3,5-diiodo-*t*-butylbenzene (0.49)	**2a** (73)
4	**6a** (0.86)	1,3,5-triiodobenzene (0.27)	**3a** (71)
5	**6a** (1.01)	tris(4-iodophenyl)amine (0.28)	**4** (22)
6	**6b** (1.07)	3,5-diiodo-*t*-butylbenzene(0.50)	**2b** (47)
7	**6b** (1.19)	1,3,5-triiodobenzene (0.37)	**3b** (47)

[a]Yield based on aryl iodide.

To obtain higher oligomers, the coupling was applied to primary amines. Although the reaction proceeded not so quantitatively as secondary amines did, excess amounts of 4-methoxyaniline was coupled with 4-iodoanisol to give tris(4-anisyl)amine **1b** (42%). Furthermore, coupling between 4-*t*-butylaniline (15 eq.) and the iodide **7**, which was obtained in the synthesis of **3a**, gave pentaamine **5**[7] (21%) as a colorless solid after purification with GPC (JAIGEL 1H + 1H, eluted with chloroform) (eq. 2).



$$ArNH_2 \xrightarrow[\text{ii) CuI}]{\text{i) BuLi}} \xrightarrow[\text{pyridine, reflux}]{\mathbf{7}} \mathbf{5} \quad \text{(eq. 2)}$$

Ar = 4-*t*-butylphenyl

To elucidate possibility of formation of the corresponding aminium radical-cations, redox properties of these amines were investigated by cyclic voltammetry at room temperature (Figure 1). The diamines **2a** and **2b** showed redox waves assignable to the corresponding mono- and bis(radical-cations) followed by further irreversible oxidation. In spite of attachment of *para*-substituent to avoid coupling of radical-cations, *meta*-connected triamines **3a**, **3b** and pentaamine **5** displayed complicated cyclic voltammograms.[8] Probably, irreversible reaction such as isomerization of bis(radical-cations) would occur via one center dication followed by intramolecular cyclization and deprotonation to generate carbazoles[9] which are easily further oxidized electrochemically at the potential (eq. 3). On the other hand, diamine **2c** and tetraamine **4** gave two and four sets of reversible waves typical of *para*-connected amines[4b] even after consecutive scanning, respectively.

Further synthetic study to obtain *meta* -connected amines with reversible redox processes and chemical oxidation and ESR study of the di-, tri-, tetra-, and pentaamines are in progress.

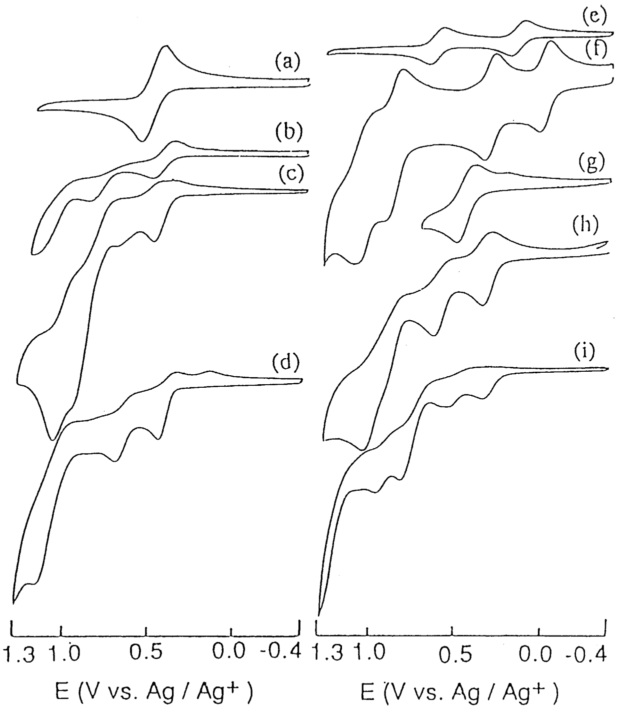
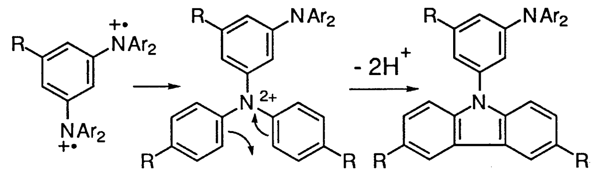


Figure 1. Cyclic voltammograms of the amines (a) **1a**, (b) **2a**, (c) **3a**, (d) **5**, (e) **2c**, (f) **4**, (g) **1b**, (h) **2b**, (i) **3b**. Solvent: CH_2Cl_2 with 0.10 M n-Bu_4NClO_4 as a support electrolyte. Working electrode: glassy carbon. Counter electrode: Pt wire. Reference electrode: Ag / 0.01 M $AgNO_3$ /0.1 M n-Bu_4NClO_4 / CH_3CN ($E_{1/2}$(Ferrocene / Ferricinim) = 0.19 V). Scan rate: 30 mV/s.



(eq. 3)

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References and Notes

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6 Copper(I) iodide, 99.5 %, available from Wako Pure Chemical Industries, Ltd., Japan, was used without further purification.

7 **5**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.175 (16H, d, J = 8.79 Hz, arom. *o*-to *t*-Bu), 7.061 (2H, d, J = 8.79 Hz, *o*-to *t*-Bu), 6.932 (16H, d, J = 8.79 Hz, arom. *o*-to N), 6.844 (2H, d, J = 8.79 Hz, arom. *o*-to N), 6.455 (2H, t, J = 1.95 Hz, *o*-to N), 6.419 (4H, d, J = 1.95 Hz, *o*- to N), 1.278 (72H, s, *t*-Bu x 8), 1.228 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.76, 148.07, 144.92, 144.70, 144.37, 128.32, 125.66, 125.15, 123.29, 120.29, 144.71, 114.05, 34.15, 33.95, 31.45; FAB-MS m/z 1417 (M^+).

8 Recently, triamine **3b** was reported to display 3 steps reversible redox process only at low temperature. See Ref. 3b. By applying narrower scan range to the *meta*-connected tri- and pentaamines, only the first redox wave became reversible and no improvement was observed concerning the waves after the second one.

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