Oligomerization of Aromatic Tertiary Amines

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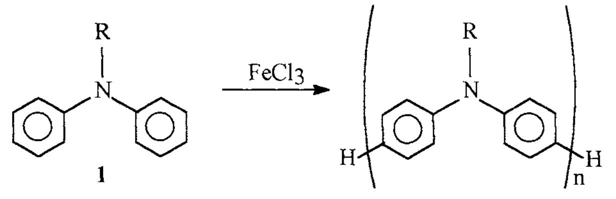
(Received October 6, 1998; CL-980770)

The oligomerization of some tertiary aromatic amines was studied using ferric chloride in a variety of solvent. The predominant dimer formation of triphenylamine (TPA) was observed in chloroform at 0 °C where concentration of TPA was 0.125 mmol/l and the molar ratio of ferric chloride to TPA was 4. Except for N-methyldiphenylamine, high molecular weight oligomers were formed in a variety of solvents.

It is commonly known that the preparation of aromatic tertiary amine oligomers has been achieved by a modified Ullmann reaction.[1,2] However, this copper metal catalyzed Ullmann reaction is typically carried out under vigorous conditions (200 °C), utilizing high boiling point solvents that results in yield[3,4] ranging from 40 to 80%. We have developed a new route of preparation for tertiary amine oligomers. In this paper we present the synthesis of oligomers obtained from a variety of substituted tertiary amines with the general structure **1** by oxidation in the presence of ferric chloride. This type of oligomers have good hole-transporting characteristics[3-5] and could find applications in thermally stable organic electroluminescent devices.



1	R
TPA	C_6H_5
p-TDPA	p-$CH_3(C_6H_4)$
m-TDPA	m-$CH_3(C_6H_4)$
MDPA	CH_3

For synthesis of these oligomers, first, we explored the oxidative oligomerization of commercially available triphenylamine (TPA) in a variety of solvents at 40 °C. The concentration of TPA was 0.25 mol/l and the molar ratio of $FeCl_3$ to TPA was 4. Oligomer formation was monitored by gel-permeation chromatography (GPC). As shown in Table 1, oligomerization proceeded in all solvents. The yield did not appear to depend on the reaction time after one hour. The higher conversions were obtained in chloroform and benzene. In chloroform, the highest yield of dimer (N,N,N',N'-tetraphenyl-1,1'-biphenyl-4,4'-diamine; TPD) was observed. More favored dimer formation (yield; 95%) was observed when the lower concentration of TPA (0.125 mol/l) and the lower temperature (0-20 °C) were utilized. Whereas, in propylene carbonate or benzene, oligomers having $n \geq 5$ were produced in a higher yield. In other solvents, a large amount of unreacted monomer was observed.

For p-tolyldiphenylamine (p-TDPA) which was synthesized according to the literature[11], high conversions were observed in chloroform and propylene carbonate and high molecular weight oligomers were obtained in all solvents we examined, especially in chloroform and propylene carbonate using standards conditions. By increasing the molar ratio of $FeCl_3$ to 6 and decreasing the monomer concentration to 0.125 mol/l, the yield of dimer (N,N'-diphenyl-N,N'-bis(4-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine;p-TDPD) increased to 90 % in the temperature range of 0-40 °C in chloroform. Chemical structure of p-TDPD was confirmed by ^1H- and ^{13}C-NMR spectroscopy.

m-Tolyldiphenylamine (m-TDPA) was also prepared according to the literature.[11] In this case, any solvent did not afford a manifest high conversion as shown in Table I. However, the yield of higher oligomers ($n \geq 5$) was higher than that observed for TPA. Although the experimental conditions affording a selective formation of dimer could not be found, the yield of dimer slightly increased to 43 % in chloroform by lowering the monomer concentration to 0.083 mol/l and temperature to 0 °C and the increase of molar ratio of $FeCl_3$ to 6. The product was purified by column chromatography (silica gel, hexane/toluene=3/1) to get a dimer. The structure of dimer was deduced on the basis of ^1H and ^{13}C NMR spectra. According to NMR analyses, the dimer consists three isomers, which resulted from the coupling at different positions on aromatic rings.

The oligomerization of commercially available methyldiphenylamine (MDPA) were performed in a similar way to the above TPA reaction, and results were tabulated in Table 1. Lower conversions were observed in DMSO, benzene and chloroform compared with the other amines. High molecular weight of oligomers ($n \geq 4$) was difficult to form for this monomer. Higher dimer yields was observed in acetonitrile and propylene carbonate. Oligomerization behavior of MDPA is found to be different from those observed for the other tertiary amines. This is probably due to the difference in basicity of each amine. TPA, p-TDPA and m-TDPA are less basic than MDPA because the nitrogen lone pair electrons are more delocalized by orbital overlap with the aromatic ring π electron system and are less available for bonding. On the other hand, in MDPA, the lone pair electrons are more localized on the nitrogen atom. MDPA can form the salt with hydrogen chloride, which is produced in the oxidative coupling reaction using $FeCl_3$, whereas triarylamines can not.[12] Salt formation should also affect the subsequent coupling reactions.

Our simple method permits the preparation of oligomers from a variety of substituted amines in mild

Table 1. Percentage of oligomers obtained by oxidation of triarylamines (**1**) in a variety of solvents with $FeCl_3$

Amine	n	THF	DMSO	BZ^a	CL^b	AN^c	PC^d
TPA	1	77.6	46.6	8.9	2.0	42.2	21.8
	2	19.1	20.7	53.3	84.2	46.5	25.3
	3	1.9	9.6	7.2	4.6	9.3	15.9
	4	1.4	10.3	11.9	4.6	2.0	16.3
	≥5	0	12.7	18.6	4.6	0	20.7
p-TDPA	1	63.7	77.0	30.9	9.4	41.9	16.9
	2	27.9	13.2	50.6	47.2	43.8	39.5
	3	9.5	4.0	12.4	12.7	8.5	23.0
	≥4	8.9	5.8	6.1	30.7	5.8	20.6
m-TDPA	1	55.8	63.7	24.9	38.2	21.8	28.8
	2	17.3	13.8	29.6	35.6	24.6	30.0
	3	3.2	3.5	6.1	9.5	15.3	10.3
	4	3.0	3.1	6.5	4.7	13.7	8.5
	≥5	20.7	15.9	32.9	12.0	24.6	22.4
MDPA	1	43.5	96.8	80.0	61.3	30.7	28.7
	2	28.8	3.2	20.0	34.8	47.1	44.4
	3	20.3	0	0	3.9	17.3	20.0
	≥4	7.4	0	0	0	4.9	6.9

Reaction time ;1.0 h, temperature ;40 °C, concentration of amine ;0.25 mmol/l, molar ratio; $FeCl_3$/**1** = 4. Oligomers are marked by *n*, number of repeating units. ^{a}benzene, ^{b}chloroform, ^{c}acetonitrile, ^{d}propylene carbonate.

conditions. The oxidative coupling of tertiary aromatic amines proceeded rapidly and readily by ferric chloride. Except for MDPA, dimer products were favored in chloroform. The optimum reaction conditions to synthesize dimers from TPA, p-TDPA are as follows: in the temperature range of 0-20 °C, the concentration of amine 0.125 mol/l in chloroform, the molar ratio $FeCl_3$/**1** = 4 for TPA or 6 for p-TDPA.

A typical synthesis of TPD is as follows: into a dry 200 ml round-bottom flask were placed 80 ml of chloroform, 2.46 g (10 mmol) of TPA. After the temperature reached 0 °C, 6.48 g (40 mmol) of ferric chloride was added all at once with stirring. This mixture was stirred in ice bath for 1.0 h. After reaction the mixture was poured into methanol. The precipitate was filtered and washed with methanol and water. Then precipitate was dissolved in toluene and the insoluble part was separated by filtration. After evaporation of the toluene, a white solid of TPD was obtained, yield 2.21g (90%).

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