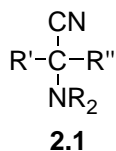


## Chapter 2

### Aromatic Polyketones from $\alpha$ -Aminonitriles

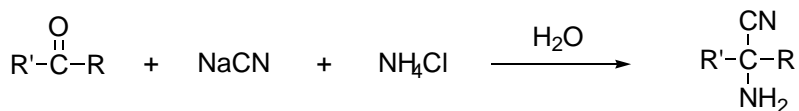
#### 2.1 Synthesis of $\alpha$ -Aminonitriles

$\alpha$ -Aminonitriles<sup>1</sup> are a class of compounds which contain the amine and nitrile functional groups on the same carbon. The general structure of  $\alpha$ -aminonitriles is represented by **2.1**. There are many ways to synthesize  $\alpha$ -aminonitriles.



$\alpha$ -Aminonitriles can be easily synthesized from aldehydes or ketones by the Strecker synthesis,<sup>2</sup> which is an efficient one step synthesis involving the use of sodium cyanide and ammonium chloride in water (Scheme 2.1). Primary or secondary amine salts can also be used to synthesize  $\alpha$ -aminonitriles.

Scheme 2.1



Another convenient aqueous synthetic method (Knoevengel-Bucherer modification<sup>3</sup>) involves the reaction of aldehydes with amines and sodium cyanide in the presence of sodium

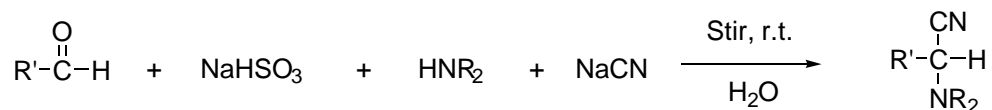
<sup>1</sup> Strecker, A. *Ann. Chem. Pharm.* **1850**, 75,27.

<sup>2</sup> March, J. *Advanced Organic Chemistry: Reactions, Mechanism, and Structure* 3<sup>rd</sup> ed. John Wiley and Sons: New York, **1985**; pp 855-856.

<sup>3</sup> Takahashi, K.; Saitoh, H.; Ogura, K.; Iida, H. *Heterocycles* **1986**, 24, 2905.

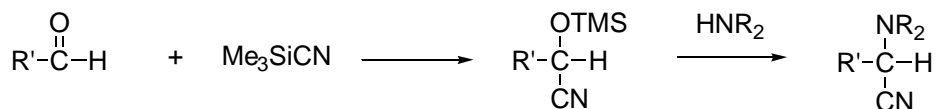
bisulfite (Scheme 2.2). Sodium bisulfite is used to form the sodium bisulfite adduct of aldehyde, which is more soluble in water and more susceptible to nucleophilic attack. The reaction products,  $\alpha$ -aminonitriles, are usually insoluble in water. This leads to high yields and easy product isolation.

**Scheme 2.2**



Alternatively,  $\alpha$ -aminonitriles can also be synthesized from trimethylsilyl cyanide and amines in anhydrous organic solvents.<sup>4,5,6</sup> The trimethylsilyl ether of the cyanohydrin is initially formed and then further reacts with amines to give the corresponding  $\alpha$ -aminonitriles (Scheme 2.3).

**Scheme 2.3**



## 2.2 Alkylation of Aryl( $\alpha$ -aminonitrile)s

$\alpha$ -Aminonitriles are analogous to the cyanohydrins, which are also acyl anion equivalents.<sup>7,8,9</sup> The acidic methine proton of  $\alpha$ -aminonitriles derived from benzaldehyde can

<sup>4</sup> Mai, K.; Patil, G. *Tet. Lett.* **1984**, 25, 4583.

<sup>5</sup> Mai, K.; Patil, G. *Syn. Comm.* **1985**, 15, 157.

<sup>6</sup> Leblanc, J.-P.; Gibson, H. W. *Tetrahedron Lett.* **1992**, 33, 6295.

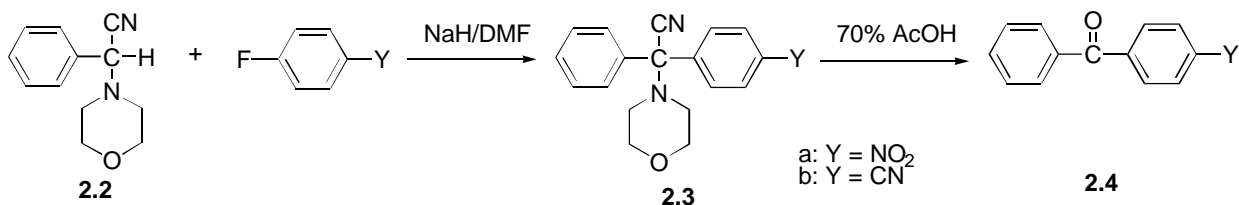
<sup>7</sup> March, J. *Advanced Organic Chemistry: Reactions, Mechanism, and Structure* 3<sup>rd</sup> ed. John Wiley and Sons: New York, **1985**; pp 859-860.

<sup>8</sup> Hauser, C. R.; Talyor, H. M.; Ledford, T. G. *J. Am. Chem. Soc.* **1960**, 82, 1786.

be easily removed using NaH as base. The corresponding conjugated base is a powerful and selective nucleophile. Alkylation, Michael addition and nucleophilic aromatic substitution have been reported.<sup>10,11</sup>

Albright and McEvoy used the  $\alpha$ -aminonitrile (**2.2**) derived from benzaldehyde and morpholine to demonstrate the reaction as an acyl anion equivalent with activated aromatic halides (Scheme 2.4). The reactions can be carried out under mild reaction conditions in DMF using sodium hydride as base. The initial reaction products **2.3** were substituted aminonitriles, which were converted in very high yields to the corresponding carbonyl compounds **2.4** by refluxing in 70% aqueous acetic acid solution.

**Scheme 2.4**



### 2.3 Wholly Aromatic Poly(ketone sulfone)s from Bis( $\alpha$ -aminonitrile)s

The  $\alpha$ -aminonitrile chemistry was first extended by our research group to make difunctional aminonitriles, which were polymerized with activated aromatic dihalides. Pandya<sup>12</sup> used bis( $\alpha$ -aminonitrile) **2.5** derived from terephthalaldehyde to polymerize with 4,4'-difluorophenyl sulfone in DMF using sodium hydride as base (Scheme 2.5). The precursor

<sup>9</sup> Stork, G.; Ozorio, A. A.; Leong, A. Y. *Tet. Lett.* **1978**, 52, 5175.

<sup>10</sup> McEvoy, F. J.; Albright, J. D. *J. Org. Chem.* **1979**, 44, 4597.

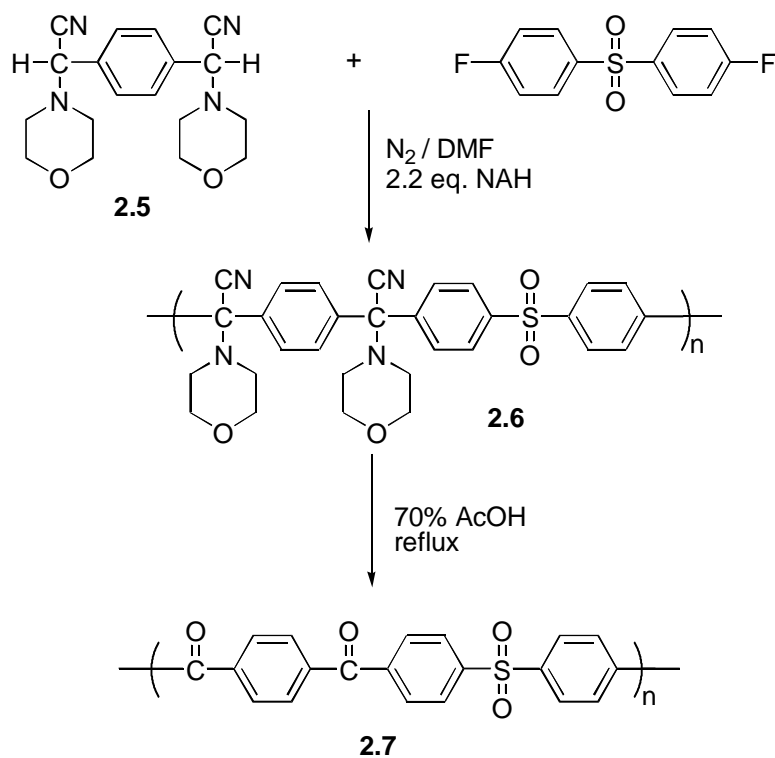
<sup>11</sup> Albright, J. D. *Tetrahedron* **1983**, 39, 3207.

<sup>12</sup> Pandya, A.; Yang, J.; Gibson, H. W. *Macromolecules* **1994**, 27, 1367.

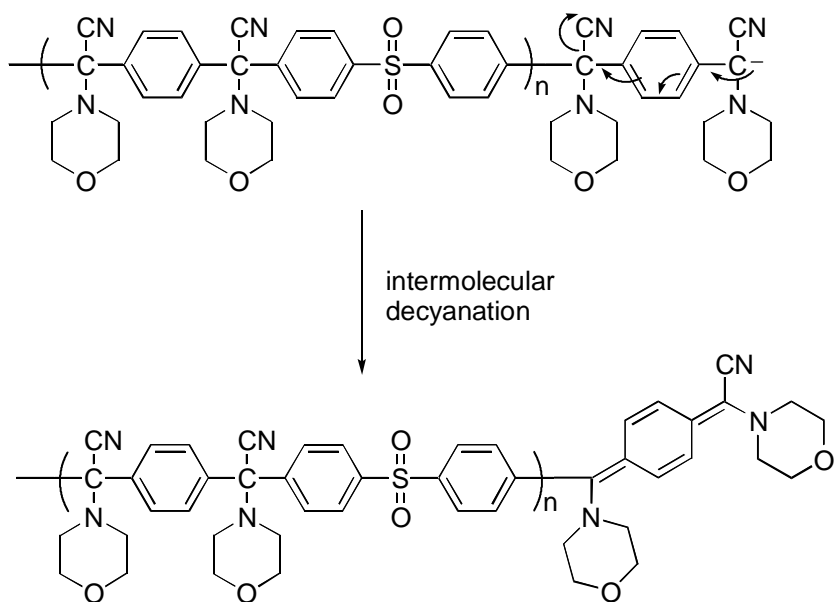
polyaminonitrile was soluble in common organic solvents, such as THF, acetone and chloroform. Hydrolysis of polymer **2.6** in 70% aqueous acetic acid yields the corresponding poly(ketone sulfone) **2.7**. Polymer **2.7** was insoluble in all common organic solvents. This polymer displayed excellent thermal stability.

The molecular weight of polymer **2.6** was relatively low (about  $M_n = 8.60$  kg/mol) due to a side reaction. The reactive chain end is an  $\alpha$ -cyanobenzyl carbanion, which could undergo an intramolecular decyanation by eliminating the good leaving group, nitrile (Scheme 2.6). This leads to loss of reactivity at the chain ends and limits the molecular weight.

**Scheme 2.5**



### Scheme 2.6



The intramolecular decyanation was eliminated when the *meta*-isomer of the bis( $\alpha$ -aminonitrile) was used. High molecular weight polyaminonitriles and polyketones were obtained using this *meta*-bis( $\alpha$ -aminonitrile). The details will be described in later chapters.

## Chapter 3

### Research Objectives and Scopes

Poly(arylene ether ketone)s are an important class of high performance engineering thermoplastics displaying excellent thermal and chemical stability and good mechanical properties. They are difficult to synthesize due to their crystallinity and the resultant low solubility in common organic solvents. The objectives of this research are to synthesize soluble, high molecular weight polyaminonitriles and then hydrolyze these precursor polymers to produce a entire new class of aromatic polyketones. Chapter 3 describes the synthesis of high molecular weight, wholly aromatic polyketones and poly(ketone sulfone)s without any ether linkages and alkyl substituents in the polymer backbones. Chapter 4 describes a very efficient approach for the synthesis of novel diphenol and activated aromatic dihalides monomers using  $\alpha$ -aminonitrile chemistry. Chapter 5 describes the synthesis of polyaminonitriles containing ether linkages in the polymer backbones and model studies.