

# Mass Fragmentation Pattern of Some Mono- and Di-Substituted Formamidines. Part-1. Mass Pattern of 1-Arylformamidines

M. Umar Ali<sup>a</sup>, M. Zahurul Haque<sup>\*b</sup>, M. Abdullah Al-Maruf<sup>a</sup> and M. Abdullah As-Saki<sup>a</sup>

<sup>a</sup> Department of Chemistry, Rajshahi University, Rajshahi-6205, Bangladesh

<sup>b</sup> BCSIR Laboratories, Rajshahi-6206, Bangladesh

(received May 20, 2004; revised February 26, 2005; accepted March 31, 2005)

**Abstract.** Some 1-arylformamidines were prepared by the Raney nickel (W-2) desulphuration of some 1-arylthioureas in anhydrous boiling benzene medium. Mass fragmentation patterns of the products were ascertained from the mass spectral data.

**Keywords:** Raney nickel, thiourea, desulphuration, mass fragmentation, 1-arylformamidines, mass pattern, nickel sulphide

## Introduction

Studies on the Raney nickel (nickel sulphide) desulphuration of organosulphur compounds are well documented. Monoarylthiocarbamides are used as starting materials for the synthesis of various substituted dithiobiurets, dithiazolidines and S-triazines (Ali *et al.*, 2001). These types of arylthiocarbamides find various industrial and biological uses (Haque *et al.*, 2003). Among the various aspects of studies on organic nitrogen and sulphur compounds, the Raney nickel desulphuration process and the chemistry of thioureas are of significant importance. The desulphuration process involving the Raney nickel has been applied in a large number of complicated syntheses. Purely as a synthetic tool, the Raney nickel desulphuration process has been used to advantage in the total synthesis of cantharidine, plumbagin, some deoxypentose and hexose derivatives, and some of their pyrimidine or purine glycosides. This catalyst, furthermore, has been employed in the structural elucidation of many complicated synthetic and natural products, such as penicillin, biotin and several other similar compounds. It has been also used in the selective desulphuration of steroid derivatives, without affecting their points of unsaturation. Raney nickel desulphuration of certain 1-arylthioureas in boiling benzene and ethanolic media has been investigated earlier (Ali and Paranjpe, 1984). The present study describes the probable mass spectral analysis of some 1-substituted arylformamidines.

## Materials and Methods

**Preparation of Raney nickel (W-2).** To an aqueous solution of caustic soda (128.0 g in 750.0 ml), powdered Ni-Al alloy (100.0 g) was added in small portions, and the system was

stirred using mechanical stirrer for a period of about 30 min. The temperature of the reaction was maintained at about 25 °C during the addition of the alloy. The system was then heated over a steambath for 5-6 h. The aqueous sodium aluminate thus formed was decanted off and the resultant Raney nickel was washed twice with water. It was again treated with a fresh solution of caustic soda (200.0 ml, 10%), and thus freed from any traces of aluminum in the form of sodium aluminate. The aqueous filtrate was decanted off and the Raney nickel so prepared was washed repeatedly with water to remove any last traces of caustic soda. It was then washed for 3-4 times with rectified spirit and was stored in the same solvent in a stoppered glass bottle (yield, 50.0 g).

### Raney nickel desulphuration of 1-chlorophenylthiourea in boiling benzene: formation of 1-*p*-chlorophenylformamidine.

To a benzene suspension of the Raney nickel (W-2; 24.0 g in 150.0 ml) in a three necked 500.0 ml round bottomed flask, fitted with a mechanical stirrer, a reflux condenser and a dropping funnel, hot benzene suspension of 1-*p*-chlorophenylthiourea (**Ia**, Fig. 1: 9.3 g, 0.05 mol in 50.0 ml) was added. The reaction mixture was heated gently to reflux, with continuous stirring for 150 min and then filtered hot to remove wasted Raney nickel (nickel sulphide). The solvent was distilled off from the filtrate and a reddish-brown solid (**IIa**, Fig. 1: 4.0 g; yield 52%) was isolated. It was washed carefully with ethanol and crystallised from a mixture of benzene-petroleum ether (1:1), m. p. 183 °C. From the elemental analysis, its molecular formula was indicated as C<sub>7</sub>H<sub>7</sub>ClN<sub>2</sub> (determined: C = 53.20, H = 4.81; N = 17.65; the expected calculated values for C<sub>7</sub>H<sub>7</sub>ClN<sub>2</sub>: C = 54.04, H = 4.53, N = 18.12%).

The product was moderately soluble in cold ethanol and chloroform but highly soluble when these solvents were hot. It

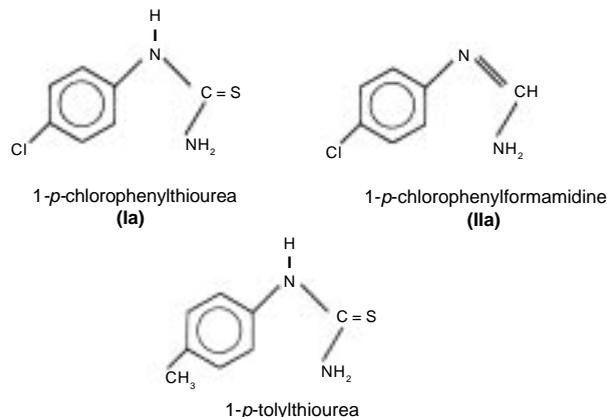
\*Author for correspondence; E-mail: mdzahurulhaque@yahoo.com

was insoluble in petroleum ether. The NMR spectrum (Dyer, 1974) of compounds **Ia** distinctly displayed signals due to the presence of amidino C-H proton ( $\delta$ , 8.07 ppm), besides those for different sets of aromatic protons ( $\delta$ , 6.90-7.32 ppm). When this Raney nickel desulphuration was extended to 1-*p*-tolylthiourea, the corresponding 1-*p*-tolylformamidine (**Ib**), m. p. 145 °C, was isolated. From the elemental analysis, its formula was indicated as  $C_8H_{10}N_2$  (determined: C = 72.18, H = 7.15, N = 20.43; the expected calculated values for  $C_8H_{10}N_2$ : C = 71.64; H = 7.46, N = 20.89). Structures of compounds **Ia**, **Ia**, as well as 1-*p*-tolylthiourea are shown in Fig. 1. The relative abundance of major ions present in the mass spectrum of compounds **Ia** and **Ib** are given in Table 1.

## Results and Discussion

The desulphuration of 1-*p*-chlorophenylthiourea (**Ia**) with Raney nickel (W-2) in boiling benzene medium and distilling out the solvent afforded a reddish solid. It was washed with ethanol carefully and crystallised from benzene-petroleum ether mixture (1:1), m.p. 183 °C. It was identified as 1-*p*-chlorophenylformamidine (**Ia**). The product was quite inert to both Fehling's and Tollen's reagents. On reaction with conc HCl in cold ethanol and aqueous picric acid it produced a hydrochloride, m.p. 316 °C and a picrate, m.p. 229 °C, respectively. When treated with bromine solution in acetic acid (10%), it furnished a N-bromo derivative, m.p. 105 °C. Besides these reactions, the product exhibited IR bands at 3280 and 1630  $cm^{-1}$ , characteristic of  $\nu$  N-H and  $\nu$  C=N functions (Katrizky, 1963; Ballamy, 1960).

The mass spectrum data showing the probable fragmentation pattern of compound **Ia**, 1-*p*-chlorophenyl-formamidine is given in Fig. 2. In Fig. 3 is given the mass spectrum data showing the probable fragmentation pattern of 1-*p*-tolylformamidine (**Ib**). The molecular ion was absent in the spectrum. In compound **Ia**, the fragmentation probably took place through two different sequences. In the first sequence, compound **Ia** lost a hydrogen radical giving rise to M-1 peak and then eliminated the terminal nitrogen to give M-15 peak. It subsequently lost a hydrogen and then a CH moiety producing M-16 and M-29 peaks, respectively. In the second fragmentation sequence, the **Ia** compound lost an amidino (NHCH=NH) moiety through a homolytic cleavage, and then eliminated the substituent chlorine radical along with a hydrogen radical, giving rise to the benzyne ( $C_6H_3$ )<sup>+</sup> cation. This ultimately was fragmented to various  $C_5$ ,  $C_4$  and  $C_3$  fractions. Besides these probable fragmentation patterns, one more peak was conspicuously observed at m/z 264. This satisfied the mass of 1,3-di-*p*-



**Fig. 1.** Structures of compounds **Ia**, **Ia**, as well as 1-*p*-tolylthiourea.

**Table 1.** Mass spectral data of compounds 1-*p*-chlorophenyl-formamidine (**Ia**) and 1-*p*-tolylformamidine (**Ib**)

Ion	<b>Ia</b>		<b>Ib</b>	
	m/z	Relative abundance* (%)	m/z	Relative abundance* (%)
(M-1H)	153	0.5	133	0.5
(M-2H)	152	0.6		
(M-3H)			131	0.8
(M-5H)	149	1.0		
(RC <sub>6</sub> H <sub>4</sub> NH=CH <sub>2</sub> )	140	5.7		
(M-NH)	139	1.7	119	0.7
(M-NH)	138	16.8	118	8.7
(M-NH <sub>2</sub> )	137	0.7	117	0.4
(RC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> +H)	128	8.4	108	7.7
(RC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> )	127	100.0	107	100.0
(RC <sub>6</sub> H <sub>4</sub> NH)	126	2.2	106	39.4
(RC <sub>6</sub> H <sub>4</sub> N)	125	1.0	105	1.1
(RC <sub>6</sub> H <sub>3</sub> N)	124	1.0	104	1.3
(RC <sub>6</sub> H <sub>5</sub> )	112	2.7	92	2.0
(RC <sub>6</sub> H <sub>4</sub> )	111	33.1	91	23.8
(RC <sub>3</sub> H <sub>4</sub> )	99	8.3	79	3.8
(C <sub>6</sub> H <sub>5</sub> )	77	2.6	77	6.2
(C <sub>6</sub> H <sub>3</sub> )	75	23.1		
(C <sub>5</sub> H <sub>5</sub> )	65	7.8	65	13.6
(C <sub>5</sub> H <sub>3</sub> )	63	6.0	63	2.2
(C <sub>4</sub> H <sub>3</sub> )	51	5.5	51	2.4
(C <sub>4</sub> H <sub>2</sub> )	50	6.2	50	0.6
(NH-CH=NH)	43	0.9		
(N-CH-N)			41	1.9
(C <sub>3</sub> H <sub>3</sub> )	39	4.9	39	4.2
(CH=NH)	28	5.0	27	0.8

\*relative abundance of the base peak has been arbitrarily taken as 100%

