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Thermal fragmentation and rearrangement of N-aryl-2-furamide oximes I

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ABSTRACT

*Thermolysis of N-aryl-2-furamide oximes **1a-c** (R=, H, CH_3 and Cl) under nitrogen gives rise to benzimidazoles as the major products (37-50%), in addition to 2-furonitrile, arylamines, 2-furoic acid, phenols, 2-furanilides, 2-(furan-2-yl)benz- oxazoles and carbazoles. In the presence of naphthalene, thermolysis of **1a** gave α- and β-naphthols (20%) beside the previous products. Also pyrolysis of **1a** in boiling tetralin lead to the formation of 1-hydroxytetralin, α-tetralone and 1,1'-bitetralyl as the major products.The isolated products have been interpreted in the terms of a free radical mechanism involving the homolysis of N-O and/or C-N bonds.*

Keywords*:* thermolysis; rearrangement; 2-furamide oximes; benzimidazoles, free radicals.

INTRODUCTION

Amidoximes in general are useful precursors for the synthesis of a variety of heterocyclic compounds [1-3]. It has previously been reported [4] that the thermolysis of benzamide oxime gave nitrogen, nitrous acid, ammonia, water, benzonitrile, benzamide, 3,5-diphenyl-1,2,4-oxadiazole, 3,5-diphenyl-1,2,4-triazole and 2,4,6-triphenyl-1,3,5-triazine. Also,Recently, we have reported that flash vacuum pyrolysis (FVP) of the benzamide oximes leads to the formation of the imino-oxadiazole as the major product and probably formed by intermolecular cycloaddition of benzonitrile oxide the diphenylcarbodiimide [5]. Moreover, thermal fragmentation and rearrangement N-arylbenzamidoximes gives benzimid- azoles, anilides, aryl amines, phenols and 2-phenylbenzoxazole [6,7].Also, Thermolysis of N-arylnicotinamide oximes under nitrogen gave rise to benzimidazoles and anilides a the major products in addition to arylamines, nicotinic acid, phenols and 2-(pyridine-3-yl) benzoxazoles [8]. Several papers have been published on the use of amidoximes as antibacterial [9], trypanocide [10] and as functional group can serve as prodrug for the amidine group [11]. The biological effects of amidoxime derivatives have prompted us to reinvestigate the thermal fragmentation of these compounds in order to gain further insight into the mechanism of fragmentation.

EXPERIMENTAL SECTION

All melting points were measured with a Gallen kamp apparatus and are uncorrected. The IR spectroscopic analyses were carried out on a Shimadzu IR-470 spectrophotometer. Analytical thin-layer chromatography was carried out on glass plates covered with silica gel (20-40 mesh), eluting acetone-pet.ether (60-80^{o}C) (1:4 v/v). Column chromatographic separations were carried out using a glass column (120 x 2.5 cm) packed with Kieselgel 60 (0.040-0.063 mm) using light petroleum-ether and ether-pentane with different ratios (1 and 2%). Gas-liquid chromatography was carried out on a Perkin-Elmer, model Sigma 3B apparatus, using a 4 ft x 4 mm column packed with SE 30 over Chromosorb W (35-80 mesh) or 10% SE 30 on Celite (60-80 mesh) at 200^{o}C, using nitrogen as a carrier gas. 1H and ^{13}C-NMR spectra for the starting materials and some reaction products were recorded using Varian EM 400 and 100 MHz instrument, respectively. GC/MS analyses were carried out using Finnigan MAT EI-

SSQ 7000 spectrophotometer with (5% phenyl)methyl polysiloxane using a 30m DB-1 capillary column. Elemental analyses were determined using a Perkin-Elmer 240 C microanalyzer. Products were identified either by co-injection with authentic materials and /or by comparison with known GC/MS library fragmentation pattern. The isolated products were separated and analyzed by IR, GLC, TLC, elemental analysis, 1H and ^{13}C-NMR, and GC/MS as compared with authentic materials.

Starting materials:

Preparation ofN-phenyl-2-furamide oxime 1a, mp 125-128ºC (Lit. [12]; mp126-128^{o}C);^{1}H-NMR (600 MHz, $CDCl_3$) δ 9.7 (s, 1H, OH), 7.37 (br, NH, 1H), 7.19(d, 1H, *J* = 7.2 Hz), 7.21 (m, 3H), 6.75 (d, 2H, *J* = 7.8), 6.56 (d, 1H, *J* = 3.6), 6.38(dd, 1H, *J* = 3.6, 1.8 Hz); MS (EI, 200^{o}C), *m/e* (%): 202 (M^+, 36.5), 185 (78), 156(36.5), 118 (22), 103 (29.2), 93 (200), 77(35.4), 65 (29.2), 51 (19.5) andelementalanalysis calculated for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85 %. Found: C,65.22; H, 5.04; N, 13.90 %.

Preparation of *N*-*p*-methylphenyl-2-furamide oxime 1b, as colourless needles, mp 158-160ºC (lit. [12], mp 160-162^{o}C); ^{1}H-NMR (600 MHz, DMSO-d_6) δ: 10.50 (s, 1H, OH), 8.24 (s, 1H, NH), 7.63 (dd, 1H, *J* = 2.4, 1.8Hz), 6.91 (d, 2H, *J* = 8.4Hz), 6.57 (m, 3H), 6.51 (dd, 1H, *J* = 3.0, 1.8Hz); MS (EI, 200^{o}C), *m/e* (%): 216 (M^+, 68.2), 199 (94), 184 (26.8), 171 (17), 117 (36.58), 107 (100), 91 (41.5), 77 (56), 65 (37.8), 51 (22); and elemental analysis calculated for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96 %. Found: C, 66.97; H , 5.48; N, 13.02 %.

Preparation of *N*-*p*-chlorophenyl-2-furamide oxime1c, mp.183-185ºC (lit [12] mp 183-184^{o}C); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 77.26 (br, 1H, NH), 7.16 (d, 2H, *J* = 2.4 ,4.8 Hz), 7.69 (d, 2H, *J*= 1.8, 4.8 Hz), 6.55 (dd, 1H, *J* = 0.6, 3.0 Hz), 6.41 (dd, 1H, *J*=1.2, 1.8Hz), 7.39 (dd, 1H, *J* = 0.6, 1.2Hz); MS (EI, 200^{o}C), m/e(%): 236 (M^+, 73), 204 (29), 184 (12), 127 (100), 99 (27), 93 (29), 75 (27), 63 (18), 51 (9) and elemental analysis calculated for $C_{11}H_9ClN_2O_2$: C, 55.83, H, 3.83, N, 11.84 %. Found: C, 55.69, H, 4.01, N, 12.12 %.

It is worth mentioning that a number of preliminary experiments were carried out to determine the proper temperature for thermolysis. The decomposition of **1a-c** starts above 220^{o}C. Also, it was found that 250^{o}C is the lowest temperatures at which the conversion of furamide oximes **1a-c** was complete at the end of thermolysis.

Thermal fragmentation of N-aryl-2-furamide oximes 1a-c:

General Procedure: The appropriate furamide oximes **1a-c**(5 g) was heated under nitrogen stream at 220-250^{o}C either alone or in naphthalene (0.5 g) as radical scavenger for 3h using a temperature-controlled heating mantle adjusted to the required temperature. The temperature was measured using a thermometer immersed in the reaction flask. The gases evolved were detected by standard chemical methods (NH_3 by Nessler's reagent). After decomposition was complete as judge by TLC monitoring, The products were separated into neutral, acidic, phenolic and basic components as in a previous work [13]. The pyrolysate was dissolved in ether and shaken several times with ethanolic potassium hydroxide solution (Claisen's solution) to dissolve the resulting phenols. The Claisen extract was acidified with 2M HCl and the liberated phenols were extracted with ether. Ether was evaporated in vacuo Phenols compounds was separated into its constituents by fractional distillation under reduced pressure, whereupon the following compounds were obtained: Phenol, collected at bp 70-5^{o}C/ 6 torr, picrate derivative, mp and mmp 83^{o}C; phenyl urethane, mp and mmp (mixed melting point) 126^{o}C and further identified by chemical test [14]. α-Naphthol, collected at 95-110^{o}C/6 torr; mp 96^{o}C and β-naphthol, collected at 150-8^{o}C/8 torr; mp and mmp 117-9^{o}C, its benzoate and picrate derivatives mp 106^{o}C and 142^{o}C, respectively; estimated by glc in the ratio 1:6 respectively and unreacted naphthalen. *p*-Cresol, collected at bp 60-65ºC/ 6 Torr; benzoyl derivative mp and mmp 71-73 ºC.*p*-Chlorophenol, collected at bp 130-5^{o}C/6 torr; mp 43-5^{o}C.2-Furoic acid, collected at bp 140-148ºC / 6 Torr; mp 128-130 ºC; MS (EI, 200^{o}C), (m/e %): 112 (100), 95 (90), 44 (5). 2-Furonitrile, collected at bp 85-92ºC/ 6 Torr; on hydrolysis gave 2-furoic acid, mp 130-132 ºC; MS ((EI, 200^{o}C), m/e % : 93 (100), 66 (40), 65 (20). 2-Furamide, collected at bp 125-130ºC/ 6 Torr; mp 138-140ºC; MS ((EI, 200^{o}C), m/e % : 111 (100), 95 (95), 67 (8), 44 (13). Aniline, collected at bp 80-86 ºC/6 Torr; acetyl derivative mp and mmp 113-114 ºC. *p*-Toluidine, collected at bp 74-78 ºC / 3 Torr; mp and mmp 45-48ºC; benzoyl derivative, mp 144-145 ºC. *p*-Chloroaniline, collected at bp 182-188ºC/ 6 Torr; mp and mmp 69-72 ºC.. The remaining residue (non-distillable) was separated by column chromatography on Kieselgel 60 ((0.040-0.063 mm) as follows: Furil was eluted using pet-ether (60-80 ºC) as eluent; mp 163-165 ºC.*N*-phenyl-2-furamide was eluted using pet. ether (60-80ºC)-benzene (1:1 v/v) as eluent; mp 122-123 ºC (lit. [15], mp 123-124ºC); IR (KBr, cm^{-1}): 3280, 3140, 3059, 1656, 1598, 1581, 1529; MS (EI, 200^{o}C), m/e (%): 187 (40), 130 (5), 95 (100), 77 (5), 65 (8), 51 (5); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 10.13 (s, 1H, NH), 7.92 (s, 1H, Ar), 7.72-7.73 (m, 2H), 7.31-7.35 (m, 3H), 7.07-7.11 (m, 1H), 6.69-7.70 (m, 1H); elemental analysis calculated for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.67; H, 4.79; N, 7.53 %. *N*-(4-Methylphenyl)-2-furamideeluted using pet-ether (60-80^{o}C) -benzene (1:1 v/v) as eluent, mp 108-110ºC (lit. [16], mp 109-110 ºC);^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.56 (dd, 1H, *J* = 3.4, 1.8 Hz), 7.17 (d, 2H, *J* = 8.2 Hz), 7.20 (d, 1H, *J* = 3.3 Hz), 7.50 (dd, 1H, *J* = 1.6, 0.7 Hz), 7.54 (d, 2H, *J* = 8.4 Hz), 8.03 (br, NH, 1H); MS (EI, 200^{o}C), m/e (%): 201 (50),

144 (5), 108 (10), 95 (100), 77 (10), 67 (5), 51 (4). *N*-(4-chlorophenyl)-2-furamide was eluted using pet. ether (60-80^{o}C)-benzene (1:1 v/v) as eluent, mp 150-152 ºC (lit. [17], mp 152-153 ºC);^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.10 (br, 1H, NH), 7.61 (d, 2H, *J* = 8.2 Hz), 7.51 (d, 1H, *J* = 1.2 Hz), 7.34 (d, 2H, *J* = 8.4 Hz), 7.25 (d, 1H, *J* = 3.6 Hz), 6.57 (dd, 1H, *J* = 1.8, 3.6 Hz);^{13}C-NMR (150 MHz, $CDCl_3$) δ: 156 (C=O amide), 147.4 (C-Fn), 144.4 (CH, Fn), 136 (C-Ph), 129.1 (2 CH-Ph), 129.5 (C-Cl), 121 (2CH-Ph), 115.6 (C-Fn), 112.7 (C-Fn);MS (EI, 200 ºC), m/e (%): 221 (M^+, 28), 95 (100), 63 (6); elemental analysis calculated for $C_{11}H_8NO_2Cl$: C, 59.61; H, 3.64; N, 6.32; Cl, 15.99 %. Found: C, 59.58; H, 3.72; N, 6.52; Cl, 15.75 %. 9H-Carbazole was eluted using pet-ether (60-80ºC)- benzene (1:2 v/v), mp 240-243 ºC (lit. [18], mp 243-245ºC); IR (KBr, cm^{-1}): 3410, 3040, 2951, 2916, 2846, 1621, 1599, 1489, 1445; ^{1}H-NMR (DMSO-d_6) δ 4.12 (s, 1H, NH), 7.17 (t, 2H, H-3, *J* = 7.7 Hz), 7.40 (t, 2H, H-2, *J* = 7.7 Hz), 7.51 (d, 2H, H-1, *J* = 7.7 Hz), 8.11 (d, 2H, H-4, *J* = 7.7 Hz); elemental Analysis calculated for ($C_{12}H_9N$): 167.0735, found: 167.0731. 3,6-Dimethyl-9H-carbazole was eluted using pet-ether (60-80 ºC)-benzene (1:2 v/v) as eluent, mp 217-219 ºC (lit. [19], mp 219-222 ºC); ^{1}H-NMR (DMSO-d_6) δ = 11.10 (s, br, 1H, NH), 9.34 (d, 2H, $H_{4,5}$ *J* = 2.3 Hz), 8.40 (dd, 2H, $H_{2,7}$, *J* = 2.3, 8.9 Hz), 7.78 (d, 2H, $H_{1,8}$, *J* = 8.9 Hz), 2.51 (s, 6H, $2CH_3$); elemental analysis calculated for $C_{14}H_{13}N$: C, 86.15; H, 6.07; N, 7.18 %. Found: C, 86.19; H, 6.69; N, 7.12 %; m/e 195. 3,6-Dichloro-9H-carbazole was eluted using light petroleum (60-80^{o}C)-benzene (1:2 v/v) as eluent, mp 202-4^{o}C (lit. [20], mp 204-206); 1HNMR (DMSO-d_6) δ 10.92 (s, br, 1H, NH), 9.14 (d, 2H, $H_{4,5}$), 8.22 (dd, 2H, $H_{2,7}$), 7.36 (d, 2H, $H_{1,8}$); m/e 236. 2-(Furan-2-yl)benz[d]oxazole was eluted using 1 % ether-pentane as eluent, mp 90-92 ºC (lit. [21], mp 88-90 ºC); IR (KBr, cm^{-1}): 3108, 1643, 1525, 1449, 1390, 1308, 1238, 1155; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.02 (s, 1H), 7.26-7.34 (m, 2H), 7.57-7.54 (m, 2H), 7.72 (dd, 1H, J = 5.9, 3.1 Hz), 8.21 (s, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 109, 110, 120, 124, 125,144.2, 144.3 (CH), 115, 142, 150, 158 (C); MS (EI, 200^{o}C), m/e (%): 185 (50), 170 (5), 103 (10), 93 (100), 77 (30), 65 (18), 51 (10); elemental analysis calculated for $C_{11}H_7NO_2$: C, 71.35; H, 3.81; N, 7.56 %. Found: C, 71.40; H, 3.78; N, 7.54 %.6-methyl-2-(furan-2-yl)benz[d]oxazole was eluted using 1% ether-pentene as eluent, mp 52-54 ºC (lit. [22], mp 53-55 ºC); m/e 199; ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.64 (dd, 1H, *J* = 2.0, 0.5 Hz), 7.34 (m, 1H, 7.50 (dd, 1H, *J* = 0.5, 3.5 Hz), 7.13-7.17 (m, 1H), 6.95 (dd, 1H, *J* = 2.0, 3.5 Hz), 8.25 (d, 1H, 8.0 Hz), 2.48 (s, 3H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 158.8, 151.4, 145, 144.7, 139.5, 135.0, 119.5, 115, 111.1, 109.6, 21.7.6-chloro-2-(furan-2-yl)benzoxazole was eluted using 1% ether-pentane as eluent, mp 136-138 ºC (lit [23]; 135-137 ºC); ^{1}H-NMR (600 MHz, $CDCl_3$): δ 6.79 (dd, 1H, *J* = 3.45, 1.76), 8.01(dd, 1H, *J* = 8.0, 0.6 Hz), 7.21 (dd, 1H, *J* = 3.45, 0.92), 7.75 (dd, 1H, *J* = 8.07, 1.81), 8.11(dd, 1H, *J* = 8.07, 0.6), 7.92 (dd, 1H, J = 1.81, 0.6); MS (EI, 200ºC), m/e (%): 220 (100), 219 (33), 204 (20), 129 (35), 127 (100), 111 (40), 94 (60), 93 (30), 75 (33). 2-(Furan-2-yl)-1H-benzimidazole was eluted using 2% ether-pentane as eluent, mp 285-287 ºC (lit. [24], mp 286-288 ºC; IR (KBr, cm^{-1}): 3442, (NH), 3093, 1625 (CN), 1521, 1438; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 12.87 (s, 1H, NH), 8.07 (d, 1H, J = 1.19 Hz), 7.47 (d, 2H, J= 1.50 Hz), 7.15-7.19 (m, 3H), 6.78 (m, 1H); MS (EI, 200^{o}C), m/e (%): 184 (100), 156 (30), 129 (18), 102 (10), 92 (12), 77 (8), 63 (10), 51 (7); elemental analysis calculated for $C_{11}H_8N_2O$: C, 71.73; H, 4.38; N, 15.21. Found: C, 71.68; H, 4.39; N, 15.48 %. 5-Methyl-2-(furan-2-yl)-1H-benzimidazole **202** was eluted using 2% ether-pentane as eluent, mp 198-200ºC (lit. [24], mp 200-202^{o}C); ^{1}H-NMR (600 MHz, DMSO-d_6) δ 2.3 (s, 3H, CH_3), 6.67 (dd, 1H, *J* = 3.4Hz), 7.83 (dd, 1H, *J* = 1.7 Hz), 7.04 (dd, 1H, *J* = 3.4 Hz), 7.11 (d, 1H, *J* = 8.12), 7.63 (d, 1H, *J* = 8.18 Hz), 7.65 (d, 1H, *J* = 4.0 Hz); MS (EI, 200^{o}C), m/e (%): 198 (100), 169 (20), 104 (8), 77 (12), 51 (7). 5-Chloro-2-(furan-2-yl)benzimidazole was eluted using 2 % ether-pentane as eluent; mp 202-203 ºC (lit. [25]; mp 200-202 ºC; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.72 (dd, 1H, *J* = 3.43, 1.75), 7.80 (dd, 1H, *J* = 1.75, 0.89), 7.03 (dd, 1H, *J* = 3.43, 0.89), 7.39 (dd, 1H, *J* = 8.06,1.69), 7.86 (dd, 1H, *J* = 8.06, 0.85), 7.83 (dd, 1H, *J* = 1.69, 0.85); MS (EI, 200 ºC), m/e (%): 218 (M^+, 100), 189 (14), 155 (36), 109 (9), 63 (12), 51 (8).

The results are given in Table 1.

Thermal fragmentation of N-phenyl-2-furamide oxime 1a in tetralin

The N-phenyl-2-furamide oxime **1a** (5 g) was placed in a 100 ml three necked flask with a gas inlet and condenser with heated under reflux at boiling anhydrous tetralin (distillation over lithium aluminum hydride under nitrogen) bp ca. 210^{o}C for 8h. The pyrolysate was evaporated in vacuo. The resulting residue was extracted with ether and was evaporated to dryness then subjected to distillation under reduced pressure, for separation of lower boiling products such as furonitrile, *p*-chlorophenol and *p*-chloroaniline as mentioned before, whereas α-tetralone was collected at bp 113-6^{o}C/6 torr; n^{20}_{D}: 1.5679; m/e 146 and 1-hydroxytetralin was collected at bp 102-5^{o}C/2 torr as pale yellow oil; n^{20}_{D}: 1.5638; phenyl urethane derivative (ligroin), mp and mmp 120-2^{o}C; m/e 148. The remaining residue was subjected to further separation into its constituents by column chromatography using ether-pentane as eluent as discussed before. 1,1'-Bitetrylal eluted from column chromatography using 2% mixture of ether-pentane, mp and mmp113^{o}C; on heating with elemental sulfur give bis-naphthylene [26]; m/e 262.

The results are summarized in Table 1.

Table 1.Thermolysis products of N-aryl-2-furamide oximes Ia-c in % yield

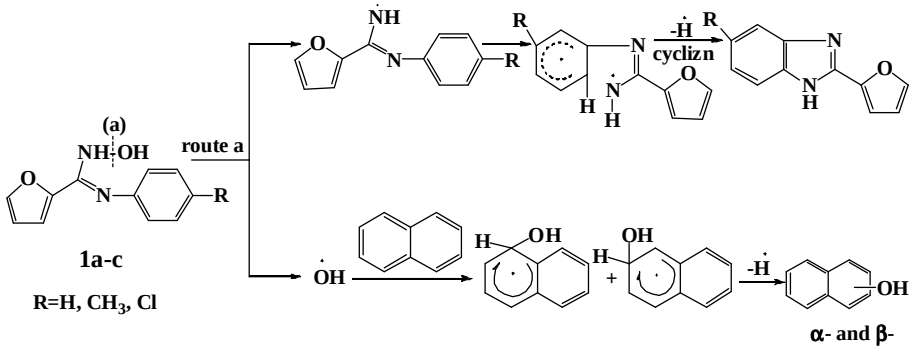
Products [a]	**Ia**, R= H	**Ib**, R= CH_3	**Ic,** R=Cl	**I**[b]
2-Furonitrile	4.1	2.5	3.1	2.1
Phenols	7.2	4.5	5.0	4.7
Furil	2.5	-	-	-
2-Furamide	1.8	-	-	-
Arylamines	8.5	5.8	5.1	4.8
Anilides	12.7	14.8	20.5	8.2
2-(Furan-2-yl) benzoxazoles	-	6.9	5.5	4.5
Benzimidazoles	45.2	46.1	52.8	40.5
2-Furoic acid	6.2	-	-	0.5
Carbazoles	7.2	6.5	5.2	1.2
α-Tetralon	-	-	-	10
1-Hydroxytetralin	-	-	-	8.2
1,1-Bitetralyl	-	-	-	15
Other products	20[c]	-	-	-
Unchanged 2-furamide oximes	(0.14)	(0.05)	(0.02)	(0.02)

a) NH_3 gas was detected by chemical means. H_2O as trace amount was separated with ether.
*b) Heating N-phenyl-2-furamide oxime **Ia** in presence of tetralin as solvent.*
*c) Heating of **Ia** in naphthalene formed α- and β-naphthols was separated as mentioned in the experimental section; estimated by GLC in the ratio 1:5, respectively.*

RESULTS AND DISCUSSION

N-phenyl-2-furamide oxime **1a** on thermolysis at 220-250^{o}C under nitrogen produced 2-(furan-2-yl)benzimidazole as major product 45.2%, in addition to furil, 2-furamide, 2-furonitrile, aniline, phenol, 9H-carbazole, 2-furoic acid,N-phenyl-2-furamide and 2-(furan-2-yl) benzoxazole as shown in Scheme 1. Although some of the products are present in small amounts due to the variable rate of decay of the free radical intermediate, their presence is of great importance for mechanistic interpretation.

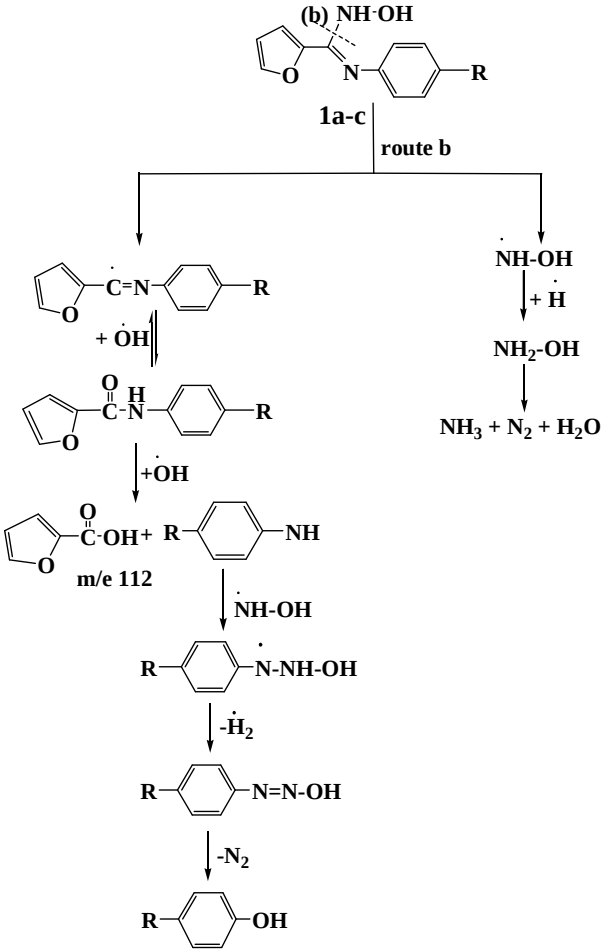
Formation of the various products can be assumed to follow the series of reactions shown in Schemes (1-6), which involves preliminary homolysis of the N-O bond (route a) [27] to form *N*-phenyl-2-furamidinyl and hydroxyl radical pairs. The furamidinyl radical undergoes intramolecular cyclization to give 2-(furan-2-yl)benzimidazole m/e l84 [28, 29] as shown in Scheme 1.



Scheme 1

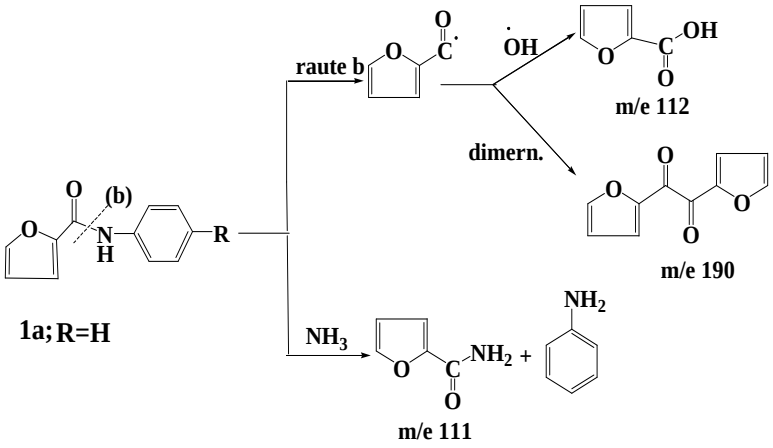
Another competing pathway for thermal fragmentation of *N*-phenyl-2- furamide oxime **1a** is the homolysis of the C-N bond (route b) leading to the formation to N-phenyl-2-furiminyl and hydroxylaminyl free radicals. The furiminyl radicals may couple with hydroxyl radicals, which are readily available in the reaction medium, to yield *N*-phenyl-2-furamide m/e 187 [30] as shown in Scheme 2. The latter compound undergoes extended hydrolysis with fragmentation under the conditions used forming 2-furoic acid m/e 112 and anilino radical [31]. The anilino radicals may couple with the hydroxyaminyl radical followed by oxidative dehydrogenation and extrusion of nitrogen to give phenol m/e 94 [32] (Scheme 2).

Moreover, the hydroxyaminyl radical (route b, Scheme 2) may abstract hydrogen from a suitable source to give hydroxylamine which ultimately decomposes into ammonia and water [31]; Scheme 2.



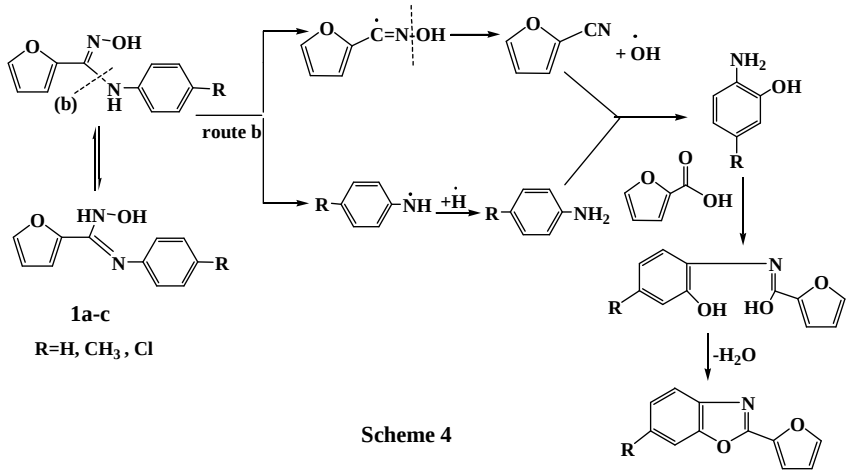
Scheme 2

On the other hand, Scheme 31 involves the homolysis of the C-N bond (route b) for thermolysis of *N*-phenyl-2-furamide under the same conditions to form 2-furoic acid m/e 123, furil m/e 190 and 2-furamide m/e 111 through furoyl and anilino radical pairs. The furoyl radicals can be considered as the precursor of the aforementioned products [30] through coupling with hydroxyl radical, dimerization and interaction with ammonia, respectively as shown in Scheme 3.



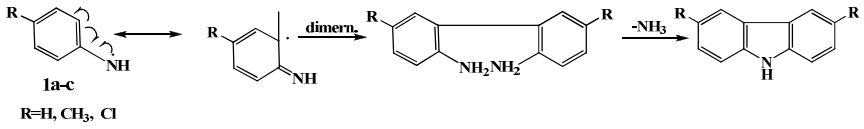
Scheme 3

Furthermore, the homolysis of the C-N bond (route b), via the tautomeric form of **1a** as reported by Tiemann [33] to give anilino and furiminoxyl radical pairs. The anilino radicals may abstract hydrogen to give aniline, whereas the furiminioxyl radicals undergo fragmentation to form 2-furonitrile and hydroxyl radicals [34], Scheme 4.
The observed absence of *o*-aminophenol can be attributed to its incorporation in the formation of 2-(furan-2-yl)benzoxozole m/e 185 which can be suggested to proceed through condensation of 2-furoic acid, which is present in the reaction medium, with *o*-aminophenol followed by elimination of water [35]; Scheme 4.



Scheme 4

The formation of 9H-carbazole m/e 167 can be explained through dimerization of anilino radicals followed by intramolecular cyclization with extrusion of ammonia[36] as shown in Scheme 5.



Scheme 5

The formation of 2-furoic acid and aniline through two routes (Schemes2, 3 and route b) may account for their high yields among the isolated products, see Table 1.

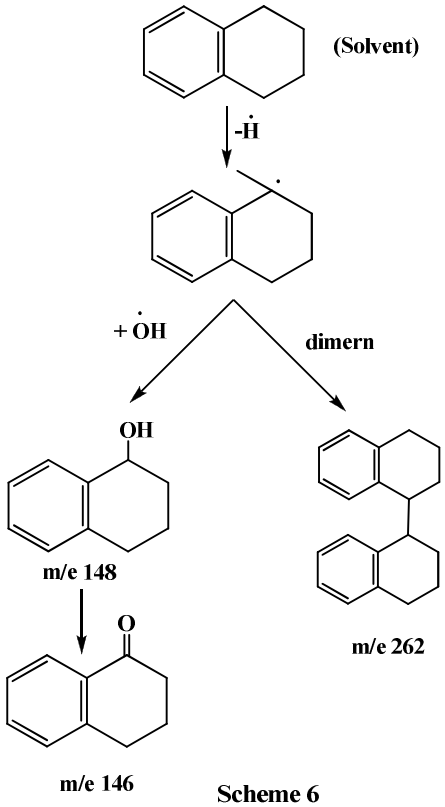
Analogous results were also obtained in the thermal fragmentation of N-p-methylphenyl-2-furamide oxime **1b** under the same conditions which gave 2-furonitrile, *p*-toluidine, *p*-cresol, 2-furoic acid, 3,6-dimethylcarbazole and in addition to 5-methyl-2-(furan-2-yl)benzimidazole and N-(4-methylphenyl)-2-furamide as the major products (46.1 and 14.8%), respectively. Such products can be interpreted with the same mechanism suggested previously as shown in Schemes 1-5.

Similar results have also obtained on thermal fragmentation of N-*p*-chlorophenyl-2-furamide oxime **1c** under the conditions used formed 2-furonitrile, *p*-chloroaniline, 2-furoic acid, *p*-chlorophenol, 3,6-dichloro-9H-carbazole beside 5-chloro-2-(furan-2-yl) benzimidazole and N-(4-chlorophenyl)-2-furamide (52.8 and 20.5%), respectively as major products as shown in Schemes 1-5.

The formation of these products can be explained similar suggested mechanism as mentioned previously in Schemes 1-5.

Attention has been given to thermal fragmentation of N-phenyl-2-furamide oxime **1a** under reflux in boiling anhydrous tetraline (210^{o}C) formed 1-hydroxytetraline, α-tetralone and 1,1'-bitetralyl as the major products beside the same products as mentioned before as shown in Schemes 1-6.

A possible pathway for the formation 1-hydroxytetralin (m/e 148), α-tetralone (m/e 146) and 1,1'-bitetralyl (m/e 262) through a process of initial hydrogen abstraction [9] from the solvent nuclei (tetralin) to form 1-tetralyl radical that interaction with hydroxyl radical which is readily available in the reaction medium followed by oxidative dehydrogenation or the 1-tetralyl radical may undergoes dimerization [31], respectively as shown in Scheme 6.



Scheme 6

It is noticed that α- and β-naphthols was absent from the pyrolysate as demonstrated by GC/MS and in Table 1. This is because the hydroxyl radical prefers to couple with 1-tetralyl radical to form 1-hydroxytetraline, hence consumption of hydroxyl radical due to the presence of other competing pathway such as H-abstraction (Scheme 6).

REFERENCES

[1] FEloy and RLenaers.*Chem. Rev.*,**1962**, 62, 166.
[2] BA Trofimov; EY Schmidt; AM Vasil'tsov; A Mikhaleva; AB Zaitsev; LVMorozova; AG Gorshkov; J Henkelman and J-D Arndt.*Synthesis*, **2001**,16, 2427.
[3] AH Moustafa.*Synthesis*,**2003**, 837.
[4] G Leandri and P Rebora. *Ann. Chim. (Rome)*,**1956**, 46, 953.
[5]AM Gaber and H McNab.*J. Anal. Appl. Pyrolysis*,**2009**, 86, 369.
[6] AM Gaber; AA Al-Ahmadi and AO Baryyan.*J. Anal. and Appl. Pyrolysis*,**2008**, 82, 110.
[7] AM Gaber; HA Muathen and LA Taib.*J. Anal. and Appl. Pyrolysis*,**2011**, 91,119.
[8]AM Gaber; HA Muathen and LA Taib.*J. Anal. and Appl. Pyrolysis*,**2012**, 93,14.
[9]RM Srivastava; AD Lima; OS Viana; MJC Silva; MTJA Catanho and JOF deMorais.*Bioorg. Med. Chem.*,**2003**, 11, 1821.
[10] ID Lamband and AC White.*J. Chem. Soc.*,**1939**, 1253.
[11] SM Rahmathullah; JE Hall; BC Bender; DR McCurdy; RR Tidwell; DW Boykin.*J. Med. Chem.*,**1999**, 42, 39.
[12]MW Partridge and HA Turner.*J. Chem. Soc.*, **1958**, 2086.
[13] Abd El-Aal M Gaber.*J. Anal. Appl. Pyrolysis*,**1998**, 47, 65.
[14] FFeigl, Spot Tests in Organic Analysis, Elsevier, Amesterdam, **1960**, p.96, 120. [15] R Gertzmann and C Guerlter.*Tetrahedron Lett.*,**2005**, 46 (39), 6659.
[16] HSuzuki; TJunko; N Sato and A Osuka.*Chem. Lett.*,**1983**, 4, 499.
[17] KL Chang; JS Yu and YR Ji.*J. Heterocyclic Chem.*,**2002**, 39, 1219.
[18] MPudlo; D Csanyi; FMoreau; G Hajos; Z Riedl and J Sapi.*Tetrahedron*,**2007**,63,10320.
[19] M Kuroki and Y Tsunashima.*J. Heterocyclic Chem.*,**1981**, 18, 709.
[20] GJ Rodriguez; RM Willamil and S Ramos. *New J. Chem.*,**1998**, 885.
[21] T Tershima; M Ishii and Y Kanaoka.*Synthesis*,**1982**, 484.
[22] RD Viirre; G Evindar and RA Batey.*J. Org. Chem.*,**2008**, 73, 3452.

[23] J Chang and S Pan.*US Patent* ,**2005**, 6, 861, 533 B2.
[24] GR Jadhav; MU Shaikh; RP Kale; CH Hill.*Chin. Chem. Lett.*,**2009**, 20, 535.
[25] DA Benson; I Karsch-Mizrachi; DJ Lipman; J Ostell; BA Rapp and DLGWheeler.*Nucl. Acids Res.*,**2000**, 28 (1), 15.
[26] J von Braun and G Kirschbaum.*Chem. Ber.*,**1921**, 54, 597.
[27] RC Weast, CRC Handbook of Chemistry and Physics.**1981**, 62 nd Ed., C. R. C. Press, p 193.
[28] PD Hobbs and PD Magnus.*J. Chem. Soc., Perkin I.*,**1973**, 469.
[29]AM Gaber; TI El-Emary and AA Atalla.*Heteroatom Chem.*,**1997**, 8(4),287.
[30] MZA Badr; MM Aly and FF Abdel-Latif.*J. Org. Chem.*,**1979**, 44, 3244.
[31] AM Gaber and N Nahas.*Afinidad*,**2009**, 539, 252.
[32] AM Gaber and SK Mohamed. *J. Chin. Chem. Soc.*, **1998**, 45, 767.
[33] E Tiemann and P Kruger.*Chem. Ber.*,**1884**, 17, 1685; O Exnerand VJehlicka,*J. Chem. Soc., Perkin II*,**1974**, 567.
[34] AM Gaber.*J. Chem. Res.(s)*,**1998**, 288.
[35] M Terashima; M Ishii and Y Kanaoka.*Synthesis*,**1982**, 484.
[36] AM Gaber.*Pol. J. Chem.*,**1995**, 69, 1301.