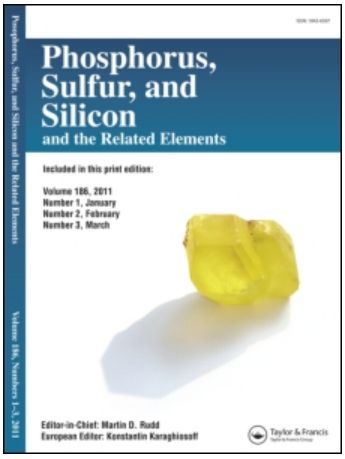


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# THERMAL FRAGMENTATION OF SOME ARYL THIOUREA DERIVATIVES

Abd El-Aal M. Gaber[a]; Omema S. Mohamed[a]
[a] Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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# THERMAL FRAGMENTATION OF SOME ARYL THIOUREA DERIVATIVES

ABD EL-AAL M. GABER* and OMEMA S. MOHAMED

*Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt*

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Thermal fragmentation of *N*-aryl-*N*-benzoylthiourea **I-III** (aryl = *p*-tolyl, 2-pyridyl, *o*-hydroxyphenyl) gave rise to benzonitrile, benzoic acid, benzamide, benzil, aryl isothiocyanate, *N,N*-diarylthiourea, the corresponding imadazoles, and anilides. A free radical mechanism has been postulated to take place through the homolysis of C-N and C-S bonds to account for the identified products.

*Keywords:* Thermolysis; Aryl thiourea; Free radicals

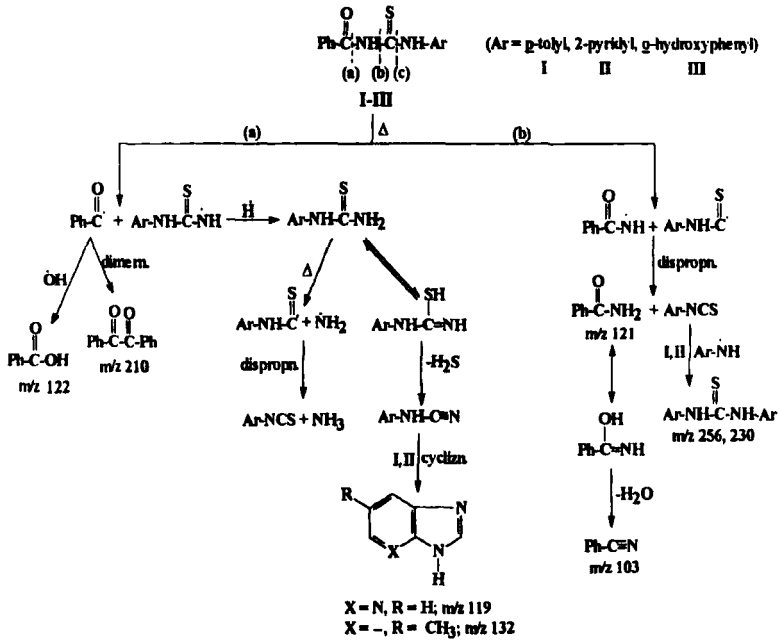
## INTRODUCTION

It is well known that thioureas decompose at high temperatures leading to the formation of different products depending on the pyrolysis conditions.[1,2] Following our interest in the thermal and photofragmentation of of some thiourea derivatives gave different products of great significant.[3,4] Decomposition of thiourea derivatives into the corresponding thiocyanates and amines are usually achieved by acid catalysis.[5] Recently,[6] the pyrolysis of 1-furoyl-3-phenylthioureas was discussed where the decomposition pyrolytic reaction that takes place through an ionization chamber.[7] Moreover, various thiourea derivatives were reported to have versatile applications in many industrial fields.[8,9] This encouraged us to carry out more experiments on the behavior of such compounds on thermolysis.

* Corresponding Author.

## RESULTS AND DISCUSSION

The present work deals with the thermolysis of *N*-*p*-tolyl-*N*-benzoylthiourea (**I**) by heating in a sealed tube in a nitrogen atmosphere at 180–200 °C for 3 h. The products were benzonitrile, benzoic acid, benzamide, benzil, *p*-toluanilide, *N*,*N*-di-*p*-tolylthiourea, benzoylisothiocyanate, and 5-methylbenzimidazole as shown in Scheme 1.



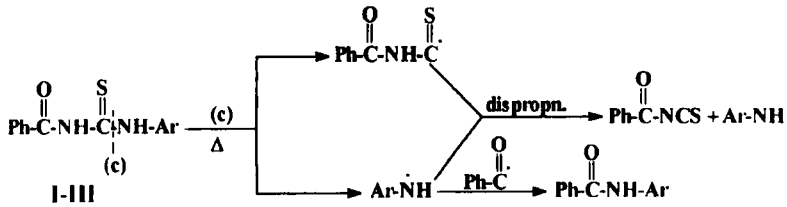

SCHEME 1

Formation of these products can be assumed to follow the series of reactions in Scheme 1 which implies the preliminary homolysis occurs with the amidyl function (route a) to form benzoyl and *p*-tolylaminothioamidyl radical pairs. The benzoyl radicals may react with hydroxyl radicals which are readily available in the reaction medium to give benzoic acid or undergo dimerization to benzil. In contrast, *p*-tolylaminothioamidyl radicals may abstract hydrogen from a suitable source to form *p*-tolylthiourea which subsequently can decompose into ammonia and *p*-tolylisothiocy-

anate as reported earlier.[10] Moreover, *p*-tolylthiourea may undergo rearrangement to *p*-tolylisothiourea which can decompose on heating into $H_2S$ and *p*-tolylcyanamide.[11] The formation of 5-methylbenzamidazole [m/z 132] may be rationalized through heating of *p*-tolylcyanamide, possibly with an initial hydrogen shift occurring, with a subsequent intramolecular cyclization as suggested previously[12,13] (Scheme 1).

The formation of benzonitrile, benzamide, and *N,N*-di-*p*-tolylthiourea can be assumed to proceed through the homolysis of the thioamidyl function (route b) to afford phenylamidyl and *p*-tolylaminylthione radical pairs which, on disproportionation, can furnish benzamide and *p*-tolylisothiocyanate.[3] Benzamide may be considered as the precursor of benzonitrile and water[14] as shown in Scheme 1. Furthermore, *p*-tolylisothiocyanate may couple with a *p*-tolylaminyl radical in the reaction medium to produce *N,N*-di-*p*-tolylthiourea [m/z 228][15] (Scheme 1).

Another competing pathway for the thermal fragmentation of *N*-*p*-tolyl-*N*-benzoylthiourea (**I**) is the homolysis of C-N bond (route c) leading to the formation of phenylamidylthione and *p*-tolylamidyl radical pairs which, on disproportionation, can give benzoylisothiocyanate and *p*-toluidine. The latter may couple with benzoyl radical (route a) to yield *p*-toluanilide [m/z 197][16] as shown in Scheme 2.




SCHEME 2

Analogous results were also obtained in the case of the thermal rearrangement of *N*-(2-pyridyl)-*N*-benzoylthiourea (**II**) under the same conditions which produced benzoic acid, benzil, benzonitrile, 2-aminopyridine, 2-pyridyl isothiocyanate, benzamide, benzoyl isothiocyanate, *N,N*-di-2-pyridylthiourea, 2-pyridoanilide, and pyrido[1,2-*a*]imidazole as shown in Schemes 1 and 2.

Similarly, thermal fragmentation of N-(*o*-hydroxyphenyl)-*N*-benzoylthiourea (**III**) under the usual conditions gave rise to benzoic acid, benzil,

benzonitrile, o-hydroxy phenol, *o*-hydroxyphenylisothiocyanate, benzamide, benzoylisothio cyanate, and *o*-hydroxybenzanilide (Schemes 1 and 2). The formation of these observed products were assumed to take place via the same mechanism suggested previously in Schemes 1 and 2. The results are given in Table I.

TABLE I Thermolysis Products of Aryl Thiourea Derivatives **I-III** in % Yield

| *Products*[a] | *I* | *II* | *III* |
|---|---|---|---|
| Benzonitrile | 10 | 12 | 14 |
| Benzoic acid | 12 | 10 | 15 |
| Benzil | 8 | 7 | 11 |
| Benzamide | 9 | 8 | 10 |
| Amines | 10[b] | 11[c] | 12[d] |
| Aryl isothiocyanates | 7[e] | 10[f] | 11[g] |
| N,N-Di-Aryl thioureas | 11[h] | 12[i] | – |
| Anilides | 12[j] | 13[k] | 12[l] |
| Imidazoles | 10[m] | 8[n] | – |
| Recovered thioureas | 5 | 4 | 8 |
| Unresolved residue (g) | 0.3 | 0.2 | 0.4 |

a. $NH_3$ detected by Nessler's reagent and $H_2S$ detected by lead acetate. $H_2O$ formed in less than 1%.
b. *p-Toluidine.*
c. 2-aminopyridine.
d. *o*-hydroxy phenol.
e. *p*-tolylisothiocyanate.
f. 2-pyridylisothiocyanate.
g. *o*-hydroxyphenylisothio- cyanate.
h. *N,N*-Di-p-tolyl thiourea.
i. *N,N*-di-(2-pyridyl)thiourea.
j. *p*-toluanilide.
k. 2-pyridoanilide.
l. *o*-hydroxybenzanilide.
m. 5-methylbenzimidazole.
n. pyrido- [1,2-*a*]imidazole.

## EXPERIMENTAL

### General

All melting points are uncorrected. The IR spectroscopic analyses were carried out on a Pye-Unicam IR spectrometer Model Sp 3–100. $^1H$ NMR

spectra for some reaction products were obtained using an EM 390 90 MHz NMR spectrometer. Thin-layer chromatography was carried out using glass plates (10 × 3 cm) coated with silica gel (25–40 mesh) eluted with ether-pentane (1:4 v/v). Preparative column chromatography separations were performed using a glass column (120 × 2.5 cm) packed with Kieselgel 60 (0.040–0.063 mm) using gradient elution technique. GC/MS analyses were carried out using a Finnigan MAT SSQ 7000 spectrometer with 5% phenylmethylpolysiloxane in a 30 m DB-1 capillary column. Products were identified either by co-injection with authentic samples and/or by comparison with known gc/ms library fragmentation patterns.

## Starting Materials

*N*-*p*-Tolyl-*N*-benzoylthiourea (**I**), crystallized from ethanol, m.p. 160–2 °C (lit.,[17] m.p. 162 °C. *N*-(2-Pyridyl)-*N*-benzoylthiourea (**II**), crystallized from ethanol, m.p. 135–6 °C (lit.,[18] m.p. 136°C. *N*-*p*-(*o*-Hydroxyphenyl)-*N*-benzoyl thiourea (**III**), crystallized from glacial acetic acid, m.p. 145–150°C (lit.,[18] m.p. 150°C.

## General method for thermolysis of thioureas I-III

The appropriate thiourea **I-III** (0.038 mol) was heated in a sealed tube in a nitrogen atmosphere at 180–200 °C for 3 h. The gases evolved were detected by standard chemical means. The pyrolysate was subjected to distillation under reduced pressure, and the following compounds were collected: benzonitrile at b.p. 40–2 °C/ 5 Torr; $n_D^{20}$ 1.527; on hydrolysis gave benzoic acid, m.p. and mm. p. 121°C; benzoylisothiocyanate[19] at b.p. 62.5–70°C/5 Torr; $n_D^{20}$ 1.6334; *p*-tolylisothiocyanate[20] at 120–5 °C/3 Torr; m.p. 25–30 °C; $n_D^{20}$ 1.6225; it react with aniline to give *N*-phenyl-*N*-p-tolylthiourea, m.p. 141°C; 2-aminopyridine (in part) at b.p. 80–5°C/5 Torr; picrate (ethanol) m.p. and mm. p. 146 °C. The remaining residues were separated by column chromatography on Kieselgel 60 (0.040–0.063 mm) using a gradient elution technique as follow: 2-aminopyridine was eluted from column chromatography using pet. ether (40–60 °C)-(60–80 °C) (1:2 v/v), m.p. 57–60 °C; *N*-acetyl derivative m.p. and mm. p. 71 °C; benzoic acid identified by preparative tlc using pet. ether (60–80 °C)-acetone (5:1 v/v) as eluent, $R_f = 0.65$, m.p. 120–121 °C; *p*-toluidine was eluted from column chromatography using pet. ether (40–60 °C), m.p.

and mm. p. 45–7 °C; benzoyl derivative, m.p. and mm. p. 140–5 °C; benzil was eluted from column chromatography using pet. ether (40–60 °C)-benzene (1:1 v/v), m.p. and mm. p. 96°C; 2,4-dinitrophenylhydrazone derivative m.p. and mm. p. 185°C; 2-pyridoanilide[21] was eluted from column chromatography using pet. ether (60–80°C)-benzene (2:1 v/v), m.p. and mm. p. 114–6°C [*m/z* 198]; *o*-hydroxyphenylisothiocyanate[22] was eluted using pet. ether (60–80 °C)-benzene (1:2 v/v), m.p. and mm. p. 53–5°C; 2-aminophenol was eluted with successive portions of pet. ether (60–80 °C)-benzene (1:2 v/v), m.p. 174–7°C; *N*-benzoyl derivative m.p. and mm. p. 167 °C; *N,N*-di-p-tolylthiourea[23] was eluted via column chromatography using benzene, m.p. 178–180 °C [*m/z* 256]; $^1$H NMR (DMSO-$d_6$)) δ 7.0–7.3 (m, 4 H, Ar-H), 7.3–7.5 (m, 4 H, Ar-H), 2.2–2.3 (s, 6 H, 2 $CH_3$), 9.6 (s, 2 H, 2 NH); *N,N*-di-2-pyridylthiourea[24] was eluted with successive portions of benzene, m.p. and mm. p. 259°C [*m/z* 230]; $^1$H NMR (DMSO-$d_6$) δ 6.9–7.1 (m, 2 H, pyridyl-H), 7.2–7.4 (m, 4 H, pyridyl-H), 7.4–7.6 (m, 4 H, pyridyl-H), 9.5 (s, 2 H, 2 NH); *p*-toluanilide[25] was eluted from column chromatography using a mixture of *n*-hexane-ether (2:1 v/v), m.p. and mm. p. 144–5°C [*m/z* 211]; 5-methylbenzimidazole[26] was eluted from column chromatography using a mixture 2% ether- pentane m.p. and mm. p. 114–7 °C [*m/z* 132]; on oxidation with $KMnO_4$; gave the product benzimidazole 5-carboxylic acid,[27] m.p. > 300 °C; pyrido[1,2-*a*]imidazole[28] was eluted from column chromatography with successive portions of a mixture 2% ether-pentane, m.p. and mm. p. 126–8 °C [*m/z* 119]; picrate (ethanol), m.p. and mm. p. 185–6°C; $^1$H NMR (DMSO-$d_6$) δ 7.3–7.5 (m, 3 H, pyridyl-H), 5.5 (s, 1 H, CH), 9.8 (s, 1 H, NH); *o*-Hydroxybenzanilide[29] was eluted using ether, m.p. and mm.p. 167–8 °C [*m/z* 213]; O-benzoyl derivative m.p. and mm.p. 185 °C; 2-pyridylisothiocyanate[24] was eluted with successive portions of ether, m.p. 110–2 °C.



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