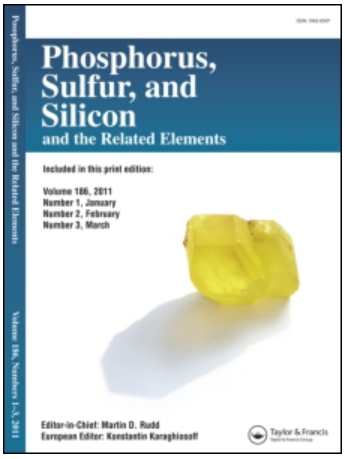

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

MOLECULAR REARRANGEMENT OF SULFUR COMPOUNDS PART (VIII)* PYROLYSIS OF ARYLTHIOSEMICARBAZIDE DERIVATIVES

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To cite this Article Atalla, A. A. , El-Dean, A. M. Kamal and Gaber, A. M.(1996) 'MOLECULAR REARRANGEMENT OF SULFUR COMPOUNDS PART (VIII)* PYROLYSIS OF ARYLTHIOSEMICARBAZIDE DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 117: 1, 205 — 212
To link to this Article: DOI: 10.1080/10426509608038787
URL: http://dx.doi.org/10.1080/10426509608038787

Phosphorus, Sulfur, and Silicon, 1996, Vol. 117, pp. 205–212
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MOLECULAR REARRANGEMENT OF SULFUR COMPOUNDS PART (VIII)* PYROLYSIS OF ARYLTHIOSEMICARBAZIDE DERIVATIVES

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(Received 7 February 1996; Revised 2 July 1996; In final form 2 July 1996)

Pyrolysis of 1,4-diarylthiosemicarbazides (1-II) by heating in a sealed tube at *ca* 200 °C give rise to NH_3,H_2S, aryl isothiocyanate, aryl amines, diarylthiocarbanilide, benzimidazole derivatives, azobenzene, aryl cyanamide and phenyl hydrazine. Similar results were obtained on pyrolysis of 1-p-chlorophenoxyacetyl-4-phenylthiosemicarbazide(III), 1-p-chlorophenoxyacetyl-4-p-tolylthiosemicarbazide(IV), and 1-acetylthiosemicarbazide(V). In addition 3,4-diaryl-5-mercapto-1,2,4-triazole was a major product. A free radical mechanism has been suggested to account for the products.

Keywords: Molecular Rearrangement; Pyrolysis; Thiosemicarbazide Derivatives

INTRODUCTION

Oxidation of 4-aryl-1-benzylidene-3-thiosemicarbazides with bromine in chloroform gave 2-benzylidene hydrazino benzothiazole, and 3,4-diaryl triazoline-5-thione[1,2]. In contrast the oxidation of 4-benzyl-3-thiosemicarbazone using bromine/acetic acid mixture gave 1,2,4-triazoline-5-thione derivative as a major product[3]. The 4-phenyl thiosemicarbazone of acetone was oxidatively cyclized in the presence of basic alumina to give 1,2,4-triazoline-5-thione[4,5].

Thermal reaction and photochemical behavior of thiosemicarbazone of glyoxil methyl ester cyclized to furnish the 3-thioxo-1,2,4-triazin-5-one and 1,2,4-triazoline derivatives.

*Part VII, Phosphorus, Sulfur, and Silicon 112; 131 (1996) Pyrolysis of Arylthiosemicarbazide Derivatives

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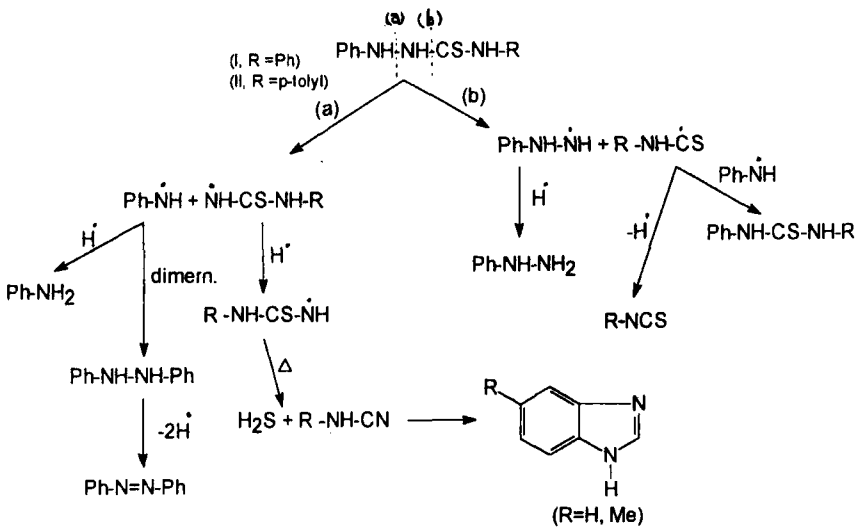
Recently[6], we have focused our effort on the thermal rearrangement of arylidene thiosemicarbazone aimed at clarification of the behavior of these compounds when subjected to the high temperature.

DISCUSSION

Pyrolysis of 1,4-diphenylthiosemicarbazide by heating in a sealed tube at 200°C for 4 hrs gave NH_3, H_2S, phenyl isothiocyanate, benzimidazole, azobenzene, aniline, thiocarbanilide, phenylcyanamide and phenylhydrazine. Formation of these products can be assumed to follow the series of reactions shown in scheme (1) which implies the preliminary homolysis of the (N--N)[7] bond route (a) forming anilino and anilinothioamidyl radical pairs. The Anilino radical may abstract hydrogen forming aniline, or dimerize to hydrazobenzene which undergoes dehydrogenation to azobenzene, whereas the anilinothioamidyl radical may abstract hydrogen to give phenylthiourea which decomposes subsequently into ammonia and phenyl isothiocyanate[8] through disproportionation.

Moreover, phenylthiourea may undergo rearrangement into phenylisothiourea which decomposes under the reaction condition into H_2S and phenyl cyanamide[9].

The formation of benzimidazole derivatives is suggested through intramolecular cyclization of aryl cyanamide[10,11] as shown in Scheme (1).



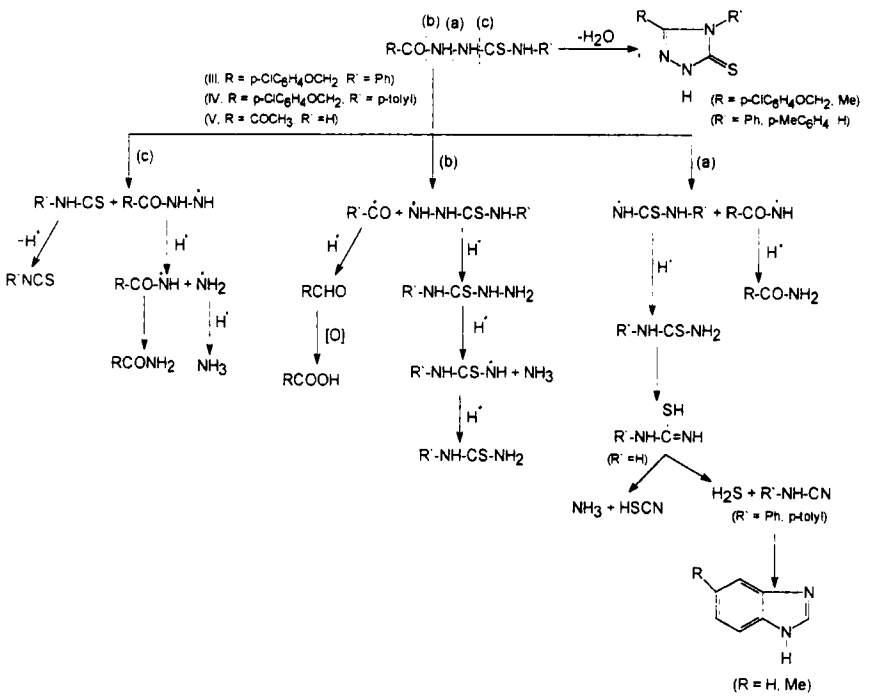
SCHEME 1

Another competing pathway involves the homolysis of (C---N) bond route (b) to give anilinothione and phenylhydrazinyl radical pairs whereby on disproportionation the former loses hydrogen to give phenyl isothiocyanate, but the latter abstracts hydrogen to form phenyl hydrazine c.f. (Scheme 1), also the anilino radical may couple with phenyl isothiocyanate to afford thiocarbanilide.

Similar results were obtained on pyrolysis of 1-phenyl-4-p-tolyl-thiosemicarbazide (II) under the present conditions, in addition to N-phenyl-N-p-tolyl thiourea, 5-methyl benzimidazole and p-tolyl isothiocyanate as shown in Scheme (1).

Pyrolysis of 1-p-chlorophenoxyacetyl-4-p-phenyl thiosemicarbazide (III), under the same reaction conditions afford 3-p-chlorophenyl-4-phenyl-5-mercapto-1,2,4 triazole as a major product besides benzimidazole, p-chlorophenoxyacetamide, p-chlorophenoxyacetic acid, phenyl isothiocyanate and phenyl cyanamide as shown in Scheme (2).

These processes involve homolysis of (N-N) bond route (a) Scheme (2) to afford p-chlorophenoxyacetamidyl and anilinothioamidyl radical pairs. The p-chlorophenoxyacetamidyl radical may abstract hydrogen to form p-chlorophenoxyacetamide while anilinothioamidyl radical may abstract hydro-



SCHEME 2

gen to furnish thiourea which ultimately rearranges to phenylisothiourea which may decompose on heating into H_2S and phenylcyanamide which is the precursor of benzimidazole through intramolecular cyclization as shown in Scheme (1).

On the other hand, Scheme (2) also includes the (C--N) homolysis route (b) to give p-chlorophenoxyacetyl and phenylthiosemicarbazidyl radical pairs. The former may abstract hydrogen to give p-chlorophenoxyacetaldehyde which oxidized with trace oxygen to form p-chlorophenoxyacetic acid, whereas phenyl thiosemicarbazidyl radical may abstract hydrogen to afford phenyl thiosemicarbazide which under the reaction condition liberates ammonia and furnish phenylthiourea which was discussed before in Scheme (1).

The formation of 3-p-chlorophenoxymethyl-4-phenyl-5-mercapto-1,2,4-triazole may be explained through tautomerization of compound (III) to the enol form followed by lose of water and intramolecular cyclization[12] c.f. Scheme (2).

Analogous results were also obtained from pyrolysis of 1-p-chlorophenoxyacetyl-4-p-tolylthiosemicarbazide (IV) at Ca. 200°C in a sealed tube leads to the formation of 3-phenoxyacetyl-4-p-tolyl-5-mercapto-1,2,4-triazole, in addition to p-chlorophenoxyacetic acid, p-tolyl isothiocyanate and 5-methylbenzimidazole c.f. Scheme (2).

Similar results obtained on pyrolysis of 1-acetyl thiosemicarbazide (V) under the same reaction conditions give rise to acetamide and thiourea which ultimatly decomposes to HNCS and ammonia[13,14], in addition to traces of 3-methyl-5-mercapto-1,2,4-triazole[15].

Finally, we can conclude that five membered heterocyclic ring formation depends on the structure of the starting thiosemicarbazide[16]. Activation of the N-(4)atom is the important step of thermal heterocyclization of the aryl thiosemicarbazides on the basis of reactivety order parallel to the basicity of the amino group.

Preparation of Reference Samples

3-p-Chlorophenoxyacetyl-4-phenyl-5-mercapto-1,2,4-triazole[17] was prepared by heating a mixture of 1-p-chlorophenoxyacetyl-4-phenyl thiosemicarbazide (0.01 mol) and NaOH (2N,20ml) under reflux for 1 hr., acedified with dilute HCl and filtered, recrystallized from ethyl alcohol m.p. 212°C, the IR spectra was in agreement with these reported in the literature[18], the presence of two strong bands around 1300 cm^{-1} showed their existance predominatly in thione form, but a weak band at 2750 cm^{-1} also indicated their presence in thiol form as well in a tautomeric mixture. The IR spectra displayed also absorption bands at 3100

cm^{-1} characteristic for free (NH), at 1600 cm^{-1} for (C–N), at 2900 cm^{-1} for (CH aliphatic) and at 3030 cm^{-1} for (CH aromatic). The ^1H NMR spectrum of s- triazole in $CDCl_3$: 6.5–7.5(m,9H,ArH), and 4.8(s,2H, OCH_3)

3-p-Chlorophenoxyacetyl-4-p-tolyl-5-mercapto-1,2,4-triazole[17] ^1H NMR in $CDCl_3$: 2.2 (s,3H,CH_3), 4.8(s,1H,OCH_2), and 6.5–7.5 (m,8H,ArH) 3-Methyl-5-mercapto-1,2,4-triazole[15].

1-Acetylthiosemicarbazide was dissolved in methyl alcohol and sodium methoxide the mixture heated overnight on steam bath, solvent removed under reduced pressure. The residue dissolved in conc. HCl, the solid washed with water and air dried, m.p. 282–283°C, m/e 115.

EXPERIMENTAL

All melting points are uncorrected. The IR spectroscopic analyses were carried out on a Pye Unicam IR spectrophotometer, Model SP 3-100. Gas Liquid chromatography was carried out using a Perkin Elmer Sigma 3B apparatus, the columns used were 4 ft × 4 mm packed with 30% SE 30 on Chromosorb W (35–80 mesh) or 10% SE on Celite (60–80 mesh) at 180°C using nitrogen as carrier gas. Thin layer chromatography was carried out by 10 × 3 cm glass plates coated with silica gel (60–80 mesh) eluting with acetone/pet. ether (60–80°C) (1:4 V/V). Column chromatographic separations were carried out using 150 × 1 cm glass columns packed with Kieselgel 60(0.040-0.030 mm) using gradient elution technique[6,10]. Molecular weight determination of some reaction products were carried out by mass spectrophotometer, Model A.E.I.M.S 902. H^1 NMR spectra for some reaction products were obtained using Varian EM-390-90 MHz NMR spectrophotometer.

Starting Materials

1,4-Diphenylthiosemicarbazide (1) m.p. 185–7°C; lit.[17] m.p. 185–187°C. 1-Phenyl-4-p-tolyl-thiosemicarbazide (II), m.p. 165°; lit.[17] m.p. 165°C. 1-p-Chlorophenoxyacetyl-4-phenylthiosemicarbazide (III), m.p. 170°C, Lit.[17] m.p. 170°C. 1-p-Chlorophenoxyacetyl-4-p-tolyl-thiosemicarbazide (IV), m.p. 166°C, Lit.[17] m.p. 166°C. 1-Acetylthiosemicarbazide (V) m.p. 165–68°C.

Structures of the pyrolysis products were assigned by a comparison with authentic samples (m.p.; IR; UV) or on the basis of analytical and spectroscopic data (IR; NMR, MS, GLC).

Pyrolysis of Thiosemicarbazide Derivatives (I–V)

General Procedure

Aryl thiosemicarbazide (10 g) was heated in a sealed tube at ca 200°C under nitrogen for 4 hrs. The products were separated as indicated in a previous work[6]. The gases evolved were detected by standard procedures; NH_3 by Nessler's reagent and H_2S by lead acetate. The pyrolysate was separated into its constituents, by fractional distillation under reduced pressure where the liquid fractions were obtained and investigated, but the remaining residue was separated by column chromatography using gradient elution technique. Products were identified by physical constants, boiling points, melting points. TLC, GLC, IR, MS as compared with authentic samples. The results are summarized in Table (I&II).

TABLE I Pyrolysis products of arylthiosemicarbazide derivatives(I–II) in g(%)

Products in g(%)	*I*	*II*
H_2S	evolved	evolved
Phenyl isothiocyanate[a]	1.5(15)	–
p-Tolyl isothiocyanate[b]	–	1.8(18)
Phenyl cyanaamide[c]	1.2(12)	–
Benzimidazole[d]	1.6(16)	–
5-Methylbenzimidazole[e]	–	2.5(25)
Aniline[f]	2.5(25)	–
Thiocarbanilide[g]	1.2(12)	–
N-Phenyl-N-p-tolylthiourea[h]	–	2.0(20)
Phenylhydrazine[i]	1.1(11)	1.5(15)
Azobenzene[j]	0.8(8)	–
p-Tolyl cyanamide[k]	–	1.7(17)

Experiments:
No. I. Pyrolysis of 1,4-diphenylthiosemicarbazide
No. II. Pyrolysis of 1-phenyl-4-p-tolylthiosemicarbazide
[a] B.p 110–5°C/10mm Hg, $^nD^{20}$ 1.6287
[b] M.p. 25–26°C, b.p. 237°C, $^nD^{20}$ 1.6345
[c] M.p. 47°C, mm.p. 46°C.
[d] M.p. 172–174°C., N-acetyl derivative m.p. 113–114°C, N-benzoyl derivative m.p. 93°C, picrate m.p. 228°C.
[e] M.p. 114°C. On oxidation with $KMnO_4$ gave benzimidazole-5-carboxylic acid.[19]
[f] B.p 180–5°C, $^nD^{20}$ 1.5815, acetyl derivative m.p. and m.m.p. 113–114°C.
[g] M.p. 152–155°C, its IR spectrum coincident with that of an au thentic sample.
[h] M.p. 141°C; with phenyl hydrazine gave 1-phenyl-4-p-tolylthiosemicarbazide, m.p. 165°C.
[i] M.p. 19°C, b.p. 238°C, $^nD^{20}$ 1.6080; N-acetyl derivative, m.p. 125–6°C., N-benzoyl derivative, m.p. 70°C.
[j] M.p. 68–69°C, and mm.p 68°C.
[k] M.p. 90°C, and mm.p 92°C.

TABLE II Pyrolysis products of 3-aryloxymethyl-4-arylhiosemicarbazide derivatives (III–V) in g(%)

Products in g(%)	*III*	*IV*	*V*
HNCS	–	–	evolved
NH3	–	–	evolved
H_2S	evolved	evolved	evolved
Phenyl isothiocyanate[a]	1.0(10)	–	–
p-Tolyl isothiocyanate[b]	–	0.8(8)	–
p-Chlorophenoxyacetamide[c]	0.6(6)	0.9(9)	–
p-Chlorophenoxyoacetic acid[d]	0.8(8)	0.6(6)	–
Acetamide[e]	–	–	3.8(38)
Benzimidazole[f]	1.2(12)	–	–
5-Methylbenzimidazole[g]	–	0.7(7)	–
Phenylcyanamide[h]	1.4(14)	–	–
p Tolylcyanamide[i]	–	1.0(10)	–
3-p-Chlorophenoxyacetyl-4-phenyl-5-mercapto-1,2,4-triazole[j]	5(50)	–	–
3-p-Chlorophenoxyacetyl-4-tolyl-5-mercapto-1,2,4-triazole[k]	–	6(60)	–
3-Methyl-5-mercapto-1,2,4-triazole[l]	–	–	1.6(16)

Experiments: No. (III). Pyrolysis of 1-p-Chlorophenoxyacetyl-4-phenylthiosemicarbazide. No. (IV). Pyrolysis of 1-p-Chlorophenoxyacetyl-4-p-tolylthiosemicarbazide. No. (V). Pyrolysis of 1-acetylthiosemicarbazide HNCS detected by chemical test[20].

[a]B.p. 110–5°C/10 mm Hg; $^nD^{20}$ 1.6287.
[b]M.p. 25–26°C, p.p 237°C, $^nD^{20}$ 1.6345.
[c]M.p. 133°C, and mm.p. 135°C.
[d]M.p. 155°C, and mm.p. 152°C.
[e]M.p. 81°C; its picrate derivative m.p. 117°C, N-acetyl derivative m.p. 79°C.
[f]M.p. 172–74°C, and mm.p. 175°C.
[g]M.p. 114°C, and m.p., mm.p. 113°C.
[h]M.p. 45°C, mm.p. 47°C.
[i]M.p. 90°C, mm.p. 92°C.
[j]M.p. 212°C, S% Calcd. 10.1, Found 10.2%.
[k]M.p. 212°C, S% Calcd. 9.7, Found 9.6%.
[l]M.p. 283°C, S% Calcd. 27.8, Found 27.8%.

Pyrolysis of Arylcyanamide

Arylcyanamide (0.01 mol) was dissolved in tetralin and the solution was refluxed at 200°C, then benzoylperoxide (0.005 mol) was added in one portion and refluxing was continued untill disappearance of benzoylperoxide [TLC: benzene/ethyl acetate (4:1 v/v)] for 6–8 h. The reaction mixture was cooled and basified by adding an aqueous solution of sodium hydrogen carbonate. The organic layer was separated, washed twice with water and dried over anhydrous sodium sulphate, after evaporation the residue was chromatographed on silica gel column with cyclohexane/ethyl acetate (4:1 v/v), the isolated product of cyclized benzimidazole derivatives (40 and 35% yield) respectively.

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