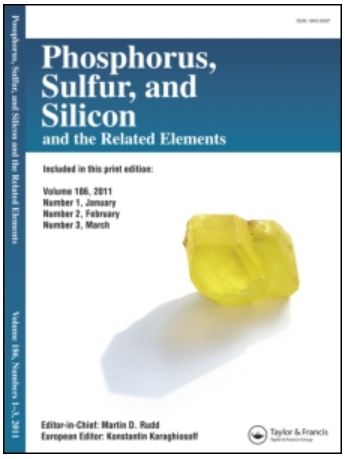

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MOLECULAR REARRANGEMENTS OF SULFUR COMPOUNDS PART VIII. PYROLYSIS OF 2-(N-SUBSTITUTED CARBOXAMIDO-METHYLTHIO)-5-ARYLAMINO-1,3,4-THIADIAZOLE DERIVATIVES

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Pyrolysis of 2-(N-substitutedcarboxamidomethylthio)-5-arylamino-1,3,4-thiadiazoles(I–III) at ca 210°C in boiling tetralin for 8 hrs or neat at ca 250°C for 5 hrs affords hydrogen sulfide, aryl isothiocyanate, arylcyanamide, benzimidazole derivatives, 4-aryl-1,2,4-triazole, thioglycolicanilides, 4-aryl-Δ^2-triazoline-5-thione and 3-aryl-2-thiohydantoin derivatives. A free radical mechanism has been suggested to account for the obtained products.

Keywords: Molecular rearrangement; pyrolysis; thiadiazole derivatives

INTRODUCTION

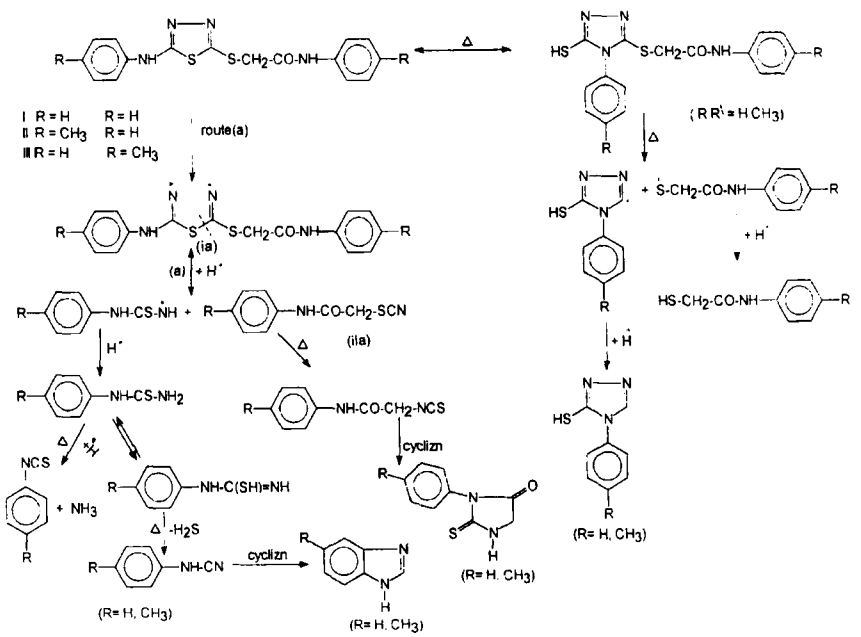
Thiadiazoles are known for their fungicidal[1–2] and insecticidal[3–5] properties. Photofragmentation of mesoionic anhydro 2,3-diaryl-5-mercapto-1,3,4-thiadiazole proceed through a valence tautomerization to yield the N-isothiocyanatothioamide in which (N-N) bond is cleaved to yield thioamide and elemental sulfur[6]. Photodecomposition of 1,3,4-thiadiazole potentially appears to involve the ethynylmercaptans, thioketene and thiirene as a transient species[7–10]

*Corresponding author.

RESULTS AND DISCUSSION

In continuation of our recent studies on the pyrolysis of organic compounds containing heteroatoms, herein we describe the behaviour of 2-(N-phenylcarboxamidomethylthio)-5-anilino-1,3,4-thiadiazole (I), 2-(N-p-tolylcarboxamidomethylthio)-5-anilino-1,3,4-thiadiazole (II) and 2-(N-phenylcarboxamidomethylthio)-5-p-toluidino-1,3,4-thiadiazole (III) on pyrolysis in anhydrous tetralin for 8 hours to give hydrogen sulfide, benzimidazole derivatives, arylcyanamide, thioglycolicanilide, 3-arylthiohydantoin and 4-aryl-1,2,4-triazole derivatives.

The process appears to involve homolytic fission of (N-N) and (C-S)[11,12] bonds according to bond dissociation energy values[13]. As shown in Scheme (1), route (a) involves the homolysis of N-N bond gives biradical (ia) which may decompose into rhodanthiocyanate (iia) and arylaminothioamidyl radical. The latter one may abstract hydrogen from the reaction medium to give aryl thiourea derivatives, which subsequently decompose into ammonia and aryl isothiocyanate[14]. Arylthiourea may undergo rearrangement into aryl isothiourea which de-



SCHEME 1

composes on heating into H_2S and arylcyanamide[15]. Moreover pyrolysis of arylcyanamide, under the reaction condition, proceeds by intramolecular cyclization to afford benzimidazole derivatives[16].

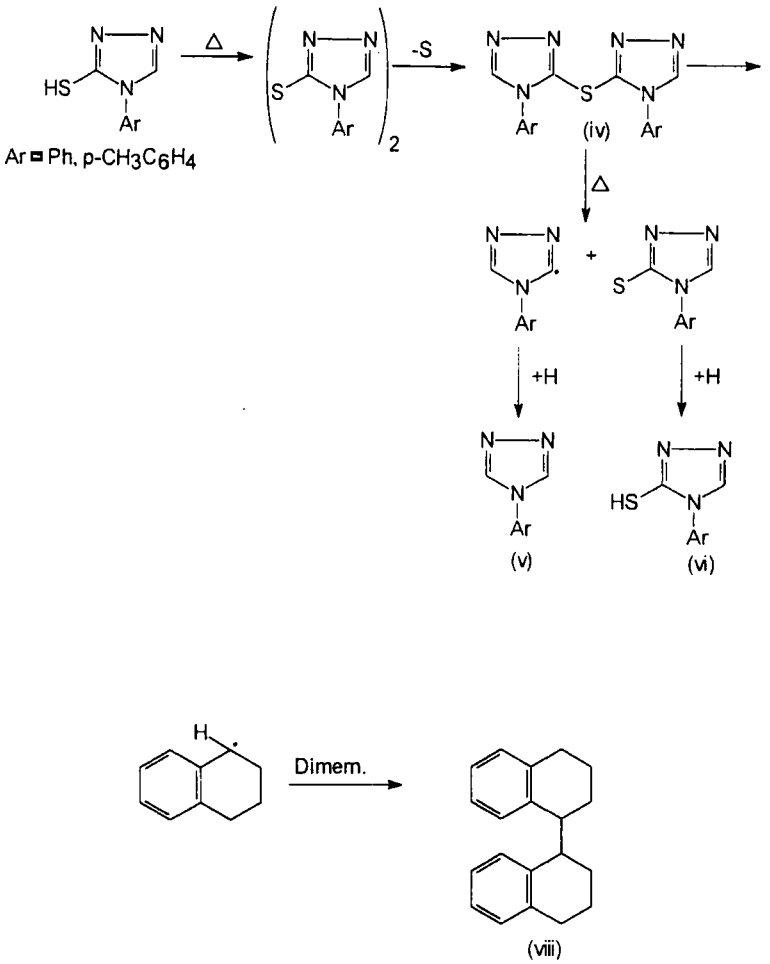
Rhodanthiocyanate (iia) which isomerizes into its isothiocyanate analogy followed by intramolecular cyclization to form 3-aryl-2-thiohydantoin[12].

Furthermore another competing pathway involves homolysis of the (C–S) bond and may afford arylaminoacetylthio and 2-arylamino-1,3,4-thiadiazole radical pairs. The former may abstract hydrogen from the reaction medium to afford thioglycolicanilide derivatives whereas 2-arylamino-1,3,4-thiadiazole radical may also abstract hydrogen to furnish 2-arylamino-1,3,4-thiadiazole. The Dimroth rearrangement[17,18] involving one side chain heteroatom is the most frequently observed rearrangement in heterocyclic chemistry. This rearrangement is either thermally included or initiated by acids or bases, therefore 2-arylamino-1,3,4-thiadiazole under the reaction conditions may rearrange to afford 4-aryl-1,2,4-triazoline-5-thione which is closely related to the rearrangements of aminotriazoles and aminotetrazoles which are the reversible isomerizations of 5-amino-1,2,3-thiadiazole into 5-mercapto-1,2,3-triazoles and of 5-amino-1,2,3,4-thiatriazoles into 1,2,3,4-tetrazoline-5-thione[19] c.f. Scheme (1). Formation of 4-aryl-1,2-4-triazole may be obtained only by heating the pure compounds (I–III) at 250°C for 5 hrs. The process may imply formation of the disulfide (iv) which loses sulfur and then suffers homolysis of the (C-S) bond to give (v, vi) radical pairs which upon hydrogen abstraction to give 4-aryl-1,2,4-triazole and 4-aryltriazoline-5-thione c.f. Scheme (2).

Coupled byproducts are formed partially through a process of initial hydrogen abstraction[20,21] from the solvent nuclei (tetralin) forming tetralyl radical intermediate which dimerizes to 1,1-ditetralyl (viii).

EXPERIMENTAL

All melting points are uncorrected, the IR spectroscopic analyses were carried out on a Shimadzu IR-470 spectrophotometer. Thin-layer chromatography was carried out on glass plates coated with silica gel 10 x 3cm, eluting with ethylacetate-benzene (1:9 v/v). Column chromatography separation was carried out using 100× 2.5 cm glass column packed with Kiesel gel 60(0.040–0.063 mm) using gradient elution technique as follows: pet ether (40–60°C), pet.ether (60–80°C)-benzene mixtures, benzene-ether mixtures, ether, ether-methanol mixtures and finally methanol. GLC analyses were carried out on a Perkin-Elmer Sigma 3B apparatus using column 4ftx 4mm packed with 30% SE 30 on



SCHEME 2

Chromosorb W(35–80 mesh) at 200°C, using nitrogen as a carrier gas. Microanalyses were performed by the Micro-analytical Units at Cairo University.

STARTING MATERIALS

2-(N-phenyl carboxamidomethylthio)-5-anilino-1,3,4-thiadiazole (I) m.p. 161–62°C, lit[22] m.p. 162–64°C.

2-(N-p.tolylcarboxamidomethylthio)-5-anilino-1,3,4-thiadiazole (II) m.p. 154°C, lit[22] m.p. 155°C.

2(N-phenylcarboxamidomethylthio)-5-p-tolyl-1,3,4-thiadiazole (III) m.p. 167°C, lit[22] m.p. 166–68°C.

Pyrolysis of 2-(N-Substituted Carboxamidomethylthio)-5-Arylamino-1,3,4-Thiadiazoles. General Procedure

The appropriate thiadiazole derivatives (I–III) (20g) was pyrolyzed in a sealed tube in the presence of nitrogen at ca 250°C for 5 hrs or refluxing in boiling tetralin for 8 hrs. The gases evolved were detected by chemical means, H_2S was identified by the lead acetate color test. The pyrolysate was separated into their constituents by means of column chromatography using gradient elution technique as mentioned above. The separated products were identified by physical constants bp., m.p, tlc, glc, ir, ^{1}H-nmr and elemental analysis and checked against authentic samples. The results are reported in table 1.

Preparation of 4-Aryl-1,2,4-Triazole by Oxidative Removal of Thioxo Group of 4-Arly-Δ^2-Triazoline-5-Thione

(0.01 mol) Of the appropriate Δ^2-triazoline-5-thione derivatives were refluxed with H_2O_2 in acetic acid for 5 hr. After cooling the precipitate was filtered off, recrystallized from alcohol to afford 4-aryl-1,2,4-triazole and identified by comparison of its ir, ^{1}H-nmr spectral data with those of an authentic sample[23].

Preparation of Reference Compounds

Phenylcyanamide[24], m.p. 45°C

p-Tolylcyanamide m.p. 69°C, recrystallized from alcohol, lit[24] m.p. 69°C

5-Methylbenzimidazole, m.p. 113°C, lit[24] m.p. 114°C, recrystallized from water.

4-p-tolyl 1,2,4-triazole, m.p. 83°C, lit[25] m.p. 83°C, its picrate derivative m.p. 172°C.

3-Phenyl-2-thiohydantoin, m.p. 200°C, synthesized by reaction of phenyl-isothiocyanate and glycine in alcoholic KOH, lit[26] m.p. 200°C.

3-p-Tolyl-2-thiohydantoin, m.p. 210°C, synthesized by reaction of p-methyl phenyl isothiocyanate and glycine in alcoholic KOH, lit[26] m.p. 210°C.

m.p. 210°C.

Thioglycolicanilide, m.p. 110°C, lit[27], m.p. 112°C. recrystallized from water.

TABLE 1 Pyrolysis products of 20g of 2-(N-substituted carboxamidomethylthio)-5-arylamino-1,3,4-thiadiazole derivatives (I-III), in gram (% yield)

Products in g(%)Expt. No	*1*	*2*	*3*
Hydrogen sulfide	evolved	evolved	evolved
Phenyl isothiocyanate[1]	0.4(2)	-	0.2(1)
p-Tolyl isothiocyanate[b]	-	0.3(1.5)	-
Benzimidazole[c]	0.2(1)	-	0.3(1.5)
5-Methylbenzimidazole[d]	-	0.4(2)	-
Phenylcyanamide[e]	0.01(0.05)	-	0.03(0.15)
p-Tolylcyanamide[f]	-	0.02(0.1)	-
3-Phenyl-2-thiohydantoin[g]	6(30	5.6(28)	-
3-p-Tolyl-2-thiohydantoin[h]	-	-	6.5(32.5)
4-Phenyl-5-thioxo-Δ^2-triazoline[i]	0.02(0.1)	-	0.01(0.05)
4-p-Tolyl-5-thioxo-Δ^2-troazp;ome[i]	-	0.02(0.1)	-
4-Phenyl-1,2,4-triazole[k]	3(15)	-	3.2(16)
4-p-Tolyl-1,2,4-triazole[l]	-	3.5(17.5)	-
Thioglycolic anilide[m]	2(10)	2.2(11)	-
Thioglycolic-p-toluidide[n]	-	-	2(10)
1,1-Ditetralyl[0]	0.02(0.1)	0.02(0.1)	0.02(0.1)
Residue	4(20)	6(30)	4(20)

Expt% (1) pyrolysis of 2-(N-phenyl carboxamidomethylthis)-5-anilino-1,3,4-thiadiazole.
(2)pyrolysis of 2-(N-p-tolyl carboxamidomethylthio)-5-anilino-1,3,4-thiadiazole.
(3)pyrolysis of 2(N-phenylcarboxamideomethylthio)-5-p-tolyl-1,3,4-thiadiazole.
[a]B.p. 221°C, $^nD^{20}$ 1.6515, it reacts with aniline to give thiocarbanilide, m.p 152–5°C
[b]B.p. 240–5°C, m.p. 25–30°C., $^nD^{20}$ 1.6225, it reacts with aniline to give N-phenyl-N-p-tolylthiourea, mp. 141°C
[c]M.p. 172–4°C,m/z 118, found N, 23.6 calcd N, 23.7.
[d]M.p. 114–7°C, b.p. 169–172°C/1mm., on oxidation with $KMnO_4$ gave benzimidazole-5-carboxylic acid.
[e]M.p. 45°C, elemental analysis, found N, 23.5 calcd N,23.7 m/z 118.
[f]M.p. 90°C, elemental analysis, found N, 21.1 calcd N,21.2 m/z 132.
[g]M.p. 200°C, elemental analysis, found S, 16.60; calcd S, 16.66%.
[h]M.p. 210°C, elemental analysis, found S, 15.53; calcd S, 15.48%.
[i]M.p. 189°C.m/z 177, found, S, 18.0 calcd, S, 18.1.
[j]M.p. 218°C.m/z 191, found, S, 16.6; calcd, S, 16.8.
[k]M.p. 121°C, its picrate derivative m.p. 169°C.
[l]M.p. 83°C, its picrate derivative m.p. 172°C.
[m]M.p. 110°C, elemental analysis, found S, 19.3; calcd S, 19.2; m/z 167.
[n]M.p. 125°C.elemental analysis, found S, 17.5; calcd S, 17.7; m/z 181.
[o]M.P. 113°C, on heating with elemental sulfur gave bis napthylen[29].

Thioglycolic-p.toluidide, m.p. 125°C lit[28] m.p. 126°C, recrystallized from alcohol.

4-Phenyl 1,2,4,-triazole, m.p. 121°C, lit[28] m.p. 122°C recrystallized from benzene, its picrate derivatives m.p. 169°C.

References

[1] R.P. Driscoll, U.S., 3, 629, 429; C.A. 76, 113228 t (1972).
[2] Schering A.G., *Neth Appl.*, **6**, 501, 398; C.A.; 66, 10130 (1970).
[3] H. Helmut and B. Friedrich, *Ger. Offen.*, **2**, 132, 019, C.A., 78, 97665s (1973).

[4] C. Tony and J. Alderman, *Ger. Offen.*, **2**, 100, 057, C. A. **75**, 799m (1971).
[5] S.S. Tiwari, A.K. Srngupta and J. Kumar, *Indian J. Pharm.*, **32**, 91, (1970).
[6] M. Moriarty and R. Mukherjee, *Tetrahedron Lett.*, 4627 (1969).
[7] A. Krantz and J. Laurent, *J. Am. Chem. Soc.*, **96**, 6768 (1974).
[8] S.A. Matlin and P.S. Sammes, *J. Chem. Soc. Chem. Commun.*, 11 (1972).
[9] P.S. Mente and C.W. Rees, *J. Chem. Soc. Chem. Commun.*, 418 (1972).
[10] J. Fenwick, G. Frater, K. Ogi and O.P. Strausz, *J. Am. Chem. Soc.*, **95**, 124 (1973).
[11] H. Quest and F. Kees, *Chem. Ber.*, **114**, 802, (1981).
[12] A.A. Atalla, A.M. Kamal El Dean, A.M. Gaber and SH.M. Radwan, *Phosphorus, Sulfur and Silicon*, **88**, 233 (1994).
[13] R.C. Weast, *Handbook of Chemistry and Physics*, C.R.C. Inc. Florida, 1982-P.F. 195.
[14] J.N. Baxter, J.C. Craige, M. Moyle and R.A. White; *J. Chem. Soc.*, 659 (1956).
[15] H. Krall, *J. Chem. Soc.*, **103**, 1378 (1913).
[16] A.M. El-Khawaga, M.F. El. Zohry, M.T. Ismail and A.A. Abd El-Wahab; *Phosphorus, Sulfur and Silicon*, **34**, 63 (1987).
[17] Review, W.D. Ollis and C.A. Ramsden, *Adv. Heterocyclic. Chem.*, **19**, 1 (1976).
[18] W.D. Ollis and C.A. Ramsden, *Chem. Commun.*, 1224 (1971); *J. Chem. Soc.*, Perkin Trans, **1**, 638 (1974).
[19] G. L'abbe, S. Toppet, G. Verhelst and C. Martens, *J. Org. Chem.*, **39**, 3770 (1974); M. Regitz and H. Scherer, *Chem. Ber.*, **102**, 417 (1969).
[20] M.Z.A. Badr and H.A.H. El Shrief, *Can. J. Chem*, **53**, 3831 (1975).
[21] A.A. Atalla, *J of Analytical and Applied Pyrolysis*, **29**, 65 (1994).
[22] A.K. Ramrakhyani, R.S. Shukla and P. Kumar, *J. Indian Chem. Chem. Soc.* Vol, 58, 8, pp. 307 (1981).
[23] M. Pesson, G. Polmanss and S. Dupin, *G.R. Acad. Sci*, Paris, **248**, 1677 (1959).
[24] F. Kurzer, *J. Chem. Soc.*, 3269 (1950).
[25] R. Ladenburg, *Ber.*, **10**, 1123 (1877).
[26] O. Aschan, *Ber.*, **17**, 424 (1884).
[27] H. Beckurts and G. Frerichs, *J. Prakt. Chem.* [2], 74, 74, 66, 174 (1941).
[28] T.L. Gilchrist, C.W. Rees and C. Thomas, *J. Chem. Soc.* Perkin Trans., **1**, 12 (1975).
[29] V. Braun and L. Kirschbaum, *Ber.*, **54**, 615 (1921).