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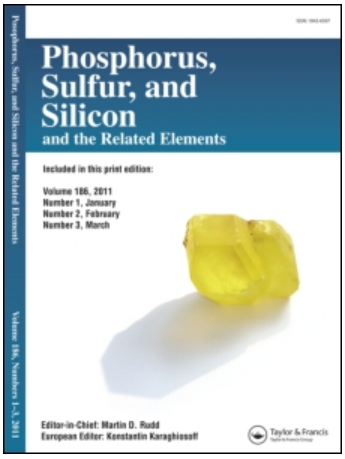

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MOLECULAR REARRANGEMENT OF SULFUR COMPOUNDS PYROLYSIS OF 2-(N-SUBSTITUTED CARBOXAMIDOMETHYLTHIO) 5-PHENYL-1,3,4-OXADIAZOLE DERIVATIVES

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MOLECULAR REARRANGEMENT OF SULFUR COMPOUNDS PYROLYSIS OF 2-(N-SUBSTITUTED CARBOXAMIDOMETHYLTHIO) 5-PHENYL-1,3,4-OXADIAZOLE DERIVATIVES

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Pyrolysis of 2-(N-phenyl carboxamidomethylthio) 5-phenyl-1,3,4-oxadiazole at ca 200°C in a sealed tube affords carbon dioxide, hydrogen sulfide, water, benzonitrile, benzamide, aniline, p-aminoacetophenone, indole, thioglycolic acid, 3-phenyl-2-thiohydantoin and 2-mercaptoquinazolinone. Furthermore pyrolysis of 2-(N-p-tolyl carboxamidomethylthio)5-phenyl-1,3,4-oxadiazole give rise to analogous products. A free radical mechanism has been suggested to account for the obtained products.

Key words: Molecular rearrangement, 2-(N-aryl carboxamidomethylthio)-5-phenyl-1,3,4-oxadiazole.

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INTRODUCTION

Molecular rearrangements[1,2] of five-membered heterocycles are conveniently classified in five categories based on the number of participating side-chain atoms. These include the rearrangements which operate by a ring contraction–ring expansion mechanism, the Dimroth rearrangement, the Cornforth rearrangement, the Boulton-Katritzky scheme, the bond-switch rearrangements with sulfur as the pivot atom, Pyrolysis of 2,4-diphenyl-1,3,4-oxadiazoline-5-one gave a nitrilimine, which in absence of a trapping agent undergoes 1,5-dipolar cyclization followed by a 1,5-sigmatropic shift to produce 3-phenylindazole.[3,4] Analgesis and anticonvulsant activities of oxadiazoles[5,6] and herbicidal[7,8] are also important.

Pyrolysis of mercapto oxadiazole and separate mercapto-quinazolinone besides other products[9] have been studied.

RESULTS AND DISCUSSION

There is continued interest in the pyrolysis of organic sulfur compounds. The behavior of 2-(N-phenylcarboxamido methyl thio) 5-phenyl-1,3,4-oxadiazoles (I), 2-(N-p-tolyl carboxamido methyl thio)-5 phenyl 1,3,4-oxadiazole (II), 2-(N-benzyl carboxamido-methyl thio)-5-phenyl-1,3,4-oxadiazole (III), which on pyrolysis at ca 200°C in a sealed tube for 2 hours gives carbon dioxide, hydrogen sulfide, water,

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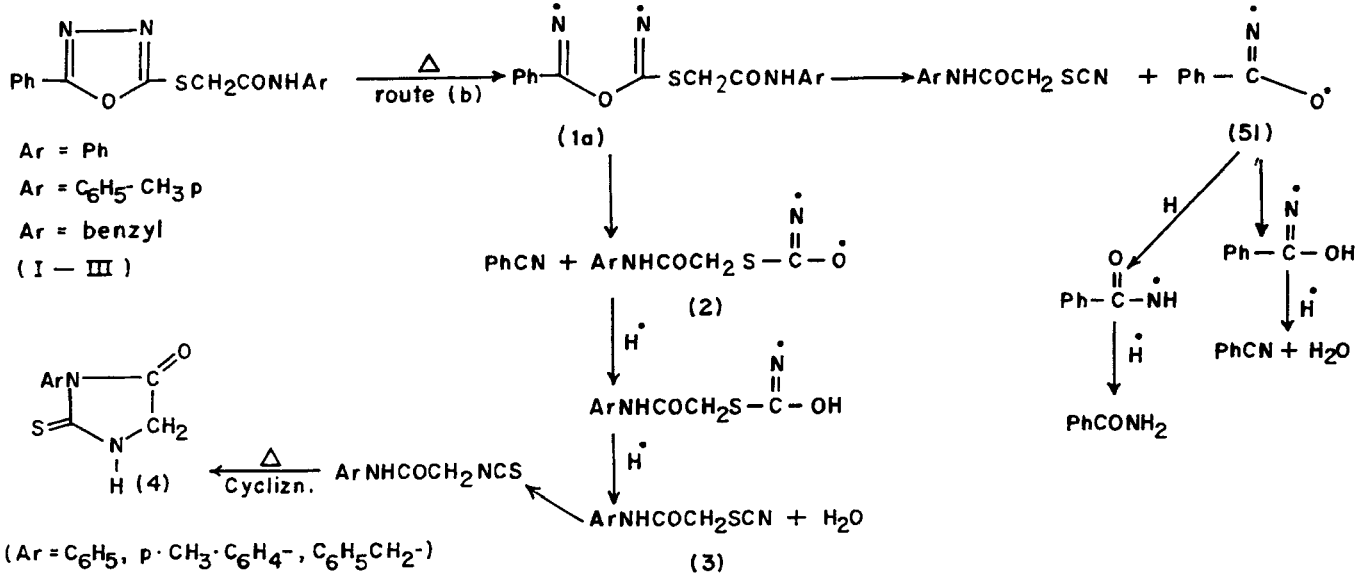

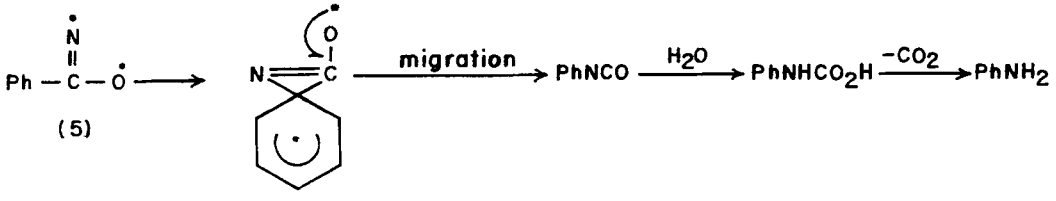

SCHEME 1

benzonitrile, benzamide, aniline, p-aminoacetophenone, indole, 2-mercaptoquinazolinone, thioglycolic acid, and 3-aryl-2-thiohydantoin is described.

On pyrolysis of (I), the process appears to involve homolytic fission of (>N—N<) and (C—S) bonds according to bond dissociation energy values.[10] Homolysis of (>N—N<) by route (a) (Scheme 1) gives the intermediate species[1,2,11] (1) which may decompose to benzonitrile and species[10] (2) which may abstract hydrogen and lose water forming rhodanthiocyanate which rearranges[12] to its isothiocyanate followed by cyclization to 3-phenyl-2-thiohydantoin (4).

Another competing pathway involves decomposition of the biradical (Ia) through (C—O) bond fission to give the rhodanthiocyanate (3) and species[1,2,11] (5) which may abstract hydrogen to afford benzamido radical which either abstracts hydrogen forming benzamide or rearranges to phenylisocyanate radical which couples with water to give aniline and carbon dioxide.

Species (5) may abstract hydrogen to give benzonitrile and water as shown in Scheme 1. Compound (I) decomposes through (C—S) bond fission route (b) to give arylaminoacetyl radical Ar—NHCOĊH_2 and 2-mercapto-5-phenyl-1,3,4 oxadiazolo radical (6).

Arylaminoacetyl radical Ar—NHCOĊH_2 may abstract hydrogen to afford acetanilide or undergoes intramolecular cyclization through elimination of water to afford indole derivatives.[13,14] Whereas 2-mercapto-5-phenyl-1,3,4 oxadiazolo radical may abstract hydrogen to give 2-mercapto-5-phenyl-1,3,4-oxadiazole, which ultimately decomposes under the same condition to give species[15] (7) which may undergo intramolecular cyclization followed by isomerization to afford 2-mercaptoquinazolinone as shown in Scheme 2.

Route (c) involves homolysis of (C—S) bond and gives rise to 5-phenyl-1,3,4-oxadiazole radical and thioglycolicanilide radical (9). The former may dimerize to 5,5-diphenyl bis 2,2-[1,3,4 oxadiazolo] and the later abstracts hydrogen and decomposes to H_2S and arylamino acetyl radical.

Pyrolysis of compound (11) under the same condition affords CO_2, H_2S, water, benzonitrile, benzamide, aniline, 6-methyl indole (8), thioglycolic acid, 2-mercaptoquinazolinone and 3-*p*-tolyl-2 thiohydantoin (4). Pyrolysis of compound (III) gave analogous products besides 3-benzyl-2 thiohydantoin (4) as a major product. The arylaminoacetyl radical under thermal conditions is the precursor for indole formation and arylaminoacetylisothiocyanate which under the same conditions afford 3-aryl 2-thiohydantoin derivatives.

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 the carrier gas. Thin-layer chromatography was carried out by a mass spectrophotometer, Model A.E.I.M.S 902.

2-(N-Phenyl carboxamidomethyl thio)-5 phenyl-1,3,4-oxadiazole (I) m.p. 138°C, lit.[16] m.p. 138–139°C

2-(N-p-tolyl carboxamidomethyl thio)-5 phenyl-1,3,4 oxadiazole (II) m.p. 145, lit.[16] m.p. 144–145°C

2-(N-Benzylcarboxamidomethyl thio)-5 phenyl 1,3,4 oxadiazole (III) m.p. 135°C, Lit.[16] m.p. 134–135°C

Pyrolysis of 2-(N-substituted carboxamidomethyl thio)-5-phenyl 1,3,4 oxadiazole

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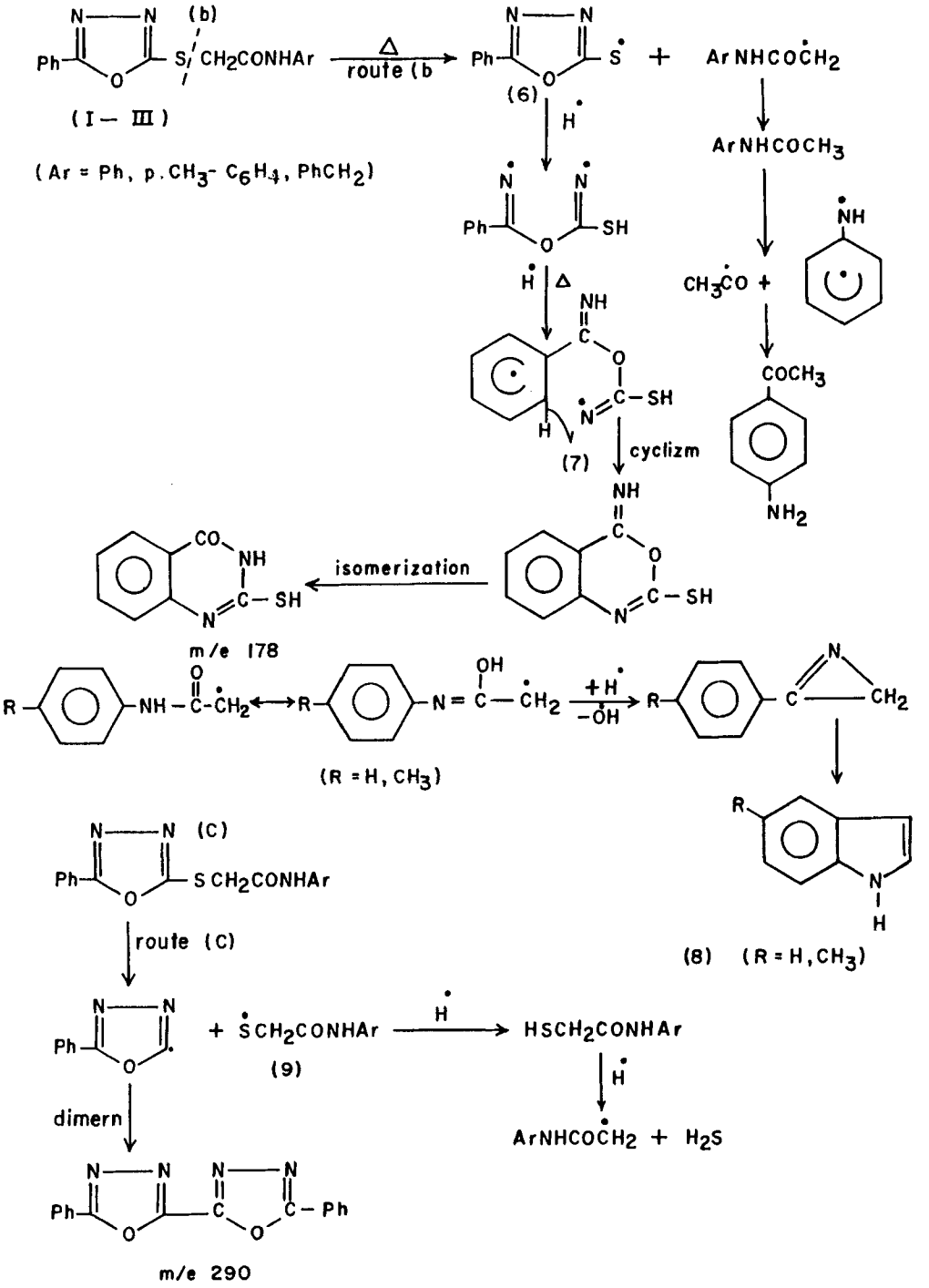

SCHEME 2

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TABLE I

Pyrolysis products of 2-(N-substituted carboxamidomethyl thio)-5-phenyl-1,3,4,-oxadiazole derivatives

Products in g (%) Expt. No.	**1**	**2**	**3**
Carbon dioxide	evolved	evolved	evolved
Hydrogen sulfide	evolved	evolved	evolved
water	traces	traces	traces
Aniline[a]	0.2(1)	0.2(1)	0.3(1.5)
Benzamide[b]	0.4(2)	0.2(1)	0.3(1.5)
p.Aminoacetophenone [c]	0.1(0.5)	-	3(1.5)
2.Merceptoquinazolinone[d]	4(20)	3(15)	0.3(1.5)
Benzonitrile[e]	0.2(1)	0.3(1.5)	0.1(0.5)
Thioglycolic acid [f]	0.1(0.5)	0.1(0.5)	0.2(0.5)
Acetanilide[g]	0.3(1.5)	0.1(0.5)	0.1(0.5)
Acetylbenzylamine [h]	-	-	0.2(1)
Indole [i]	2(10)	-	-
5. Methylindole[j]	-	3(15)	-
3.Phenyl-2 thiohydantoin[k]	8(40)	-	-
3- Benzyl-2-thiohydantoin [L]	-	-	10(50)
3p tolyl -2 thiohydation [m]	-	7(35)	-
5,5 Diphenyl bis 2,2[1,3,4 oxadiazolo	traces	traces	traces
Residue	0.1(0.5)	0.2(1)	0.1(0.5)

Expt. (I) Pyrolysis of 2.(N.Phenyl- carboxamidomethyl thiol) 5-phenyl 1,3,4-oxadiazole.

(II) Pyrolysis of 2.(N.p.tolyl carboxamidomethyl thiol) 5-phenyl 1,3,4-oxadiazole.

(III) Pyrolysis of 2.(N.benzyl carboxamidomethyl thiol) 5-phenyl 1,3,4-oxadiazole.

General procedure

2-N(substituted carboxamidomethyl thio)-5-phenyl-1,3,4-oxadiazole (20 g) was heated in a sealed tube at ca 200°C under nitrogen for 3 hrs. The products were separated as indicated in a previous work.[7] The gases evolved were detected by standard procedures, carbon dioxide by lime water or baryta solution and hydrogen sulfide by lead acetate. The pyrolysate was separated into its constituents by means of column chromatography over silica gel using gradient elution technique. The separated products were identified by physical constants, boiling points, melting points, TLC, GLC, IR and/or Ms and compared with authentic samples. The results are shown in Table I.

a) B.p. 80–85°C/13 mm Hg, $^{n}D^{20}$ 1.5836; acetyl derivative m.p. and m.p. 113–114°C.

b) M.p. 128–129°C, its IR spectrum identical with that of an authentic sample.

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c) M.p., 108°C, IR spectrum identical with that of an authentic sample.

d) M.p. 315–316°C, its structure is based on elemental, spectral and molecular ion determination analysis; found S 17.96%, N 15.17; Calc. S 17.97, N 15.73%

e) B.p. 188°C, $^{n}D^{20}$ 1.5280, on hydrolysis gives benzoic acid m.p. 120°C.

f) B.p. 96°C/5 mm. Hg, $^{n}D^{20}$ 1.5030.

g) M.p. 58°C.

h) M.p. 60°C.

i) M.p. 52°C, its picrate m.p. 187°C.

j) M.p. 58°C, its picrate m.p. 151°C.

k) M.p. 200°C, elemental analysis found S 16.60; Calc. S 16.66.

l) M.p. 128°C, elemental analysis found S 15.51; Calc. S 15.53.

m) M.p. 210°C, elemental analysis found S 15.53; Calc. S 15.53.

Preparation of reference compounds

2-Mercaptoquinazolinone, recrystallized from acetic acid mp. 315–316°C, Lit.[17] m.p. 315–316°C.

5-Methylindole m.p. 58°C, recrystallized from water, its picrate m.p. 151°C, recrystallized from hot H_2O lit.[18] m.p. 58°C.

3-Phenyl-2-thiohydantoin, m.p. 200°C synthesized by reaction of phenyl isothiocyanate and glycine in alkoholic KOH, Lit.[19] m.p. 200°C.

3-*p*-tolyl-2-thiohydantoin, m.p. 210°C, synthesized by reaction of p-tolyl isothiocyanate and glycine in alkoholic KOH, lit.[19] m.p. 210°C.

3-Benzyl-2-thiohydantoin, m.p. 128°C, synthesized by reaction of benzylisothiocyanate and glycine in alkoholic KOH, lit.[19] m.p. 128°C.

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