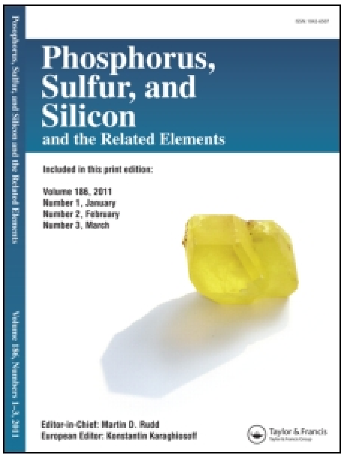

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MOLECULAR REARRANGEMENT OF SULFUR COMPOUNDS. PART V: PYROLYSIS OF MERCAPTOOXADIAZOLE DERIVATIVES

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MOLECULAR REARRANGEMENT OF SULFUR COMPOUNDS. PART V: PYROLYSIS OF MERCAPTOOXADIAZOLE DERIVATIVES

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Pyrolysis of 5-phenyl-2-benzylthio-1,3,4-oxadiazole (**1**) by heating at *ca.* 250°C in a sealed tube gives rise to CO_2, H_2S, H_2O, benzyl thiocyanate, benzonitrile, benzyl sulfide, aniline, benzamide, benzaldehyde, 2-mercaptoquinazolinone, dibenzyl, stilbene, and tetraphenylthiophene. Furthermore pyrolysis of 5-phenyl-2-phenacylthio-1,3,4-oxadiazole (**9**) gives analogous results, besides phenancyl thiocyanate. Pyrolysis of 5(2-hydroxyphenyl)-2-benzylthio-1,3,4-oxadiazole (**11**) gives 2-hydroxybenzonitrile, 5(2-hydroxyphenyl)-1,3,4-oxadiazole-2-thiol, and 2-hydroxybenzamide, in addition to the previous obtained results. The mechanism of these results has been discussed.

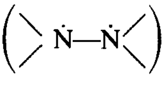
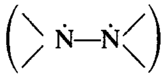
Key words: Molecular rearrangement; pyrolysis; mercaptooxadiazoles.

INTRODUCTION

The flash vacuum pyrolysis of 2-phenyl-*N*-allyl substituted-1,3,4-oxadiazolin-5-one system has been reported[1] to be a convenient source of nitrilimines, e.g. $(R{-}C{\equiv}\overset{+}{N}\overset{-}{N}R)$.[2-4] Thermolysis of 2,4-diphenyl-1,3,4-oxadiazolin-5-one gave a nitrilimine, which in absence of a trapping agent undergoes, 1,5-dipolar cyclization,[5] followed by a 1,5-sigmatropic shift to produce 3-phenylindazole.[2]

RESULTS AND DISCUSSION

We have continuing interest in pyrolysis of organic sulfur compounds.[6] Herein we describe the behaviour of 5-phenyl-2-benzylthio-1,3,4-oxadiazole (**1**) which on pyrolysis at *ca.* 250°C for 5 h gives carbon dioxide, hydrogen sulfide, water, aniline, benzonitrile, benzyl thiocyanate, benzaldehyde, benzamide, bibenzyl, stilbene, tetraphenylthiophene, and 2-mercaptoquinazolinone.

The process appear to involve homolytic fission of  and (C—S) bonds according to bond dissociation energy values.[7] However homolysis of  by route (a) gives a biradical **1a** which may decompose to benzonitrile and species **2** which may abstract hydrogen and lose water forming benzyl thiocyanate. On the other hand, another competing pathway involves decomposition of biradical **1a** through (C—O) bond fission to give benzyl thiocyanate and species

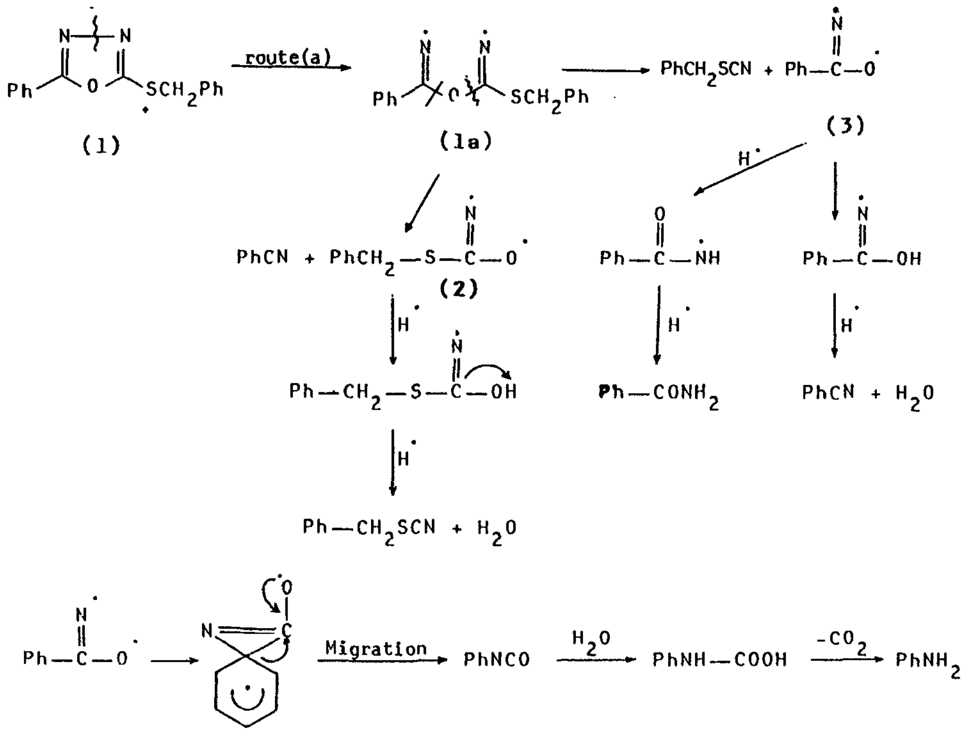
3 which may abstract hydrogen to afford a benzamido radical which either abstracts hydrogen forming benzamido rearranges[8] to a phenyl isocyanate radical which couples with water to give aniline and carbon dioxide. Species **3** abstract hydrogen to give benzonitrile and water as shown in Scheme 1.

However, compound **1** also decomposes through (C—S) bond fission route (b) to give a benzyl radical and a 2-mercapto-5-phenyl-1,3,4-oxadiazole radical (**4**). The former may dimerize to bibenzyl and undergo dehydrogenation to afford stilbene which may couple with sulfur forming 2,3,4,5-tetraphenylthiophene.

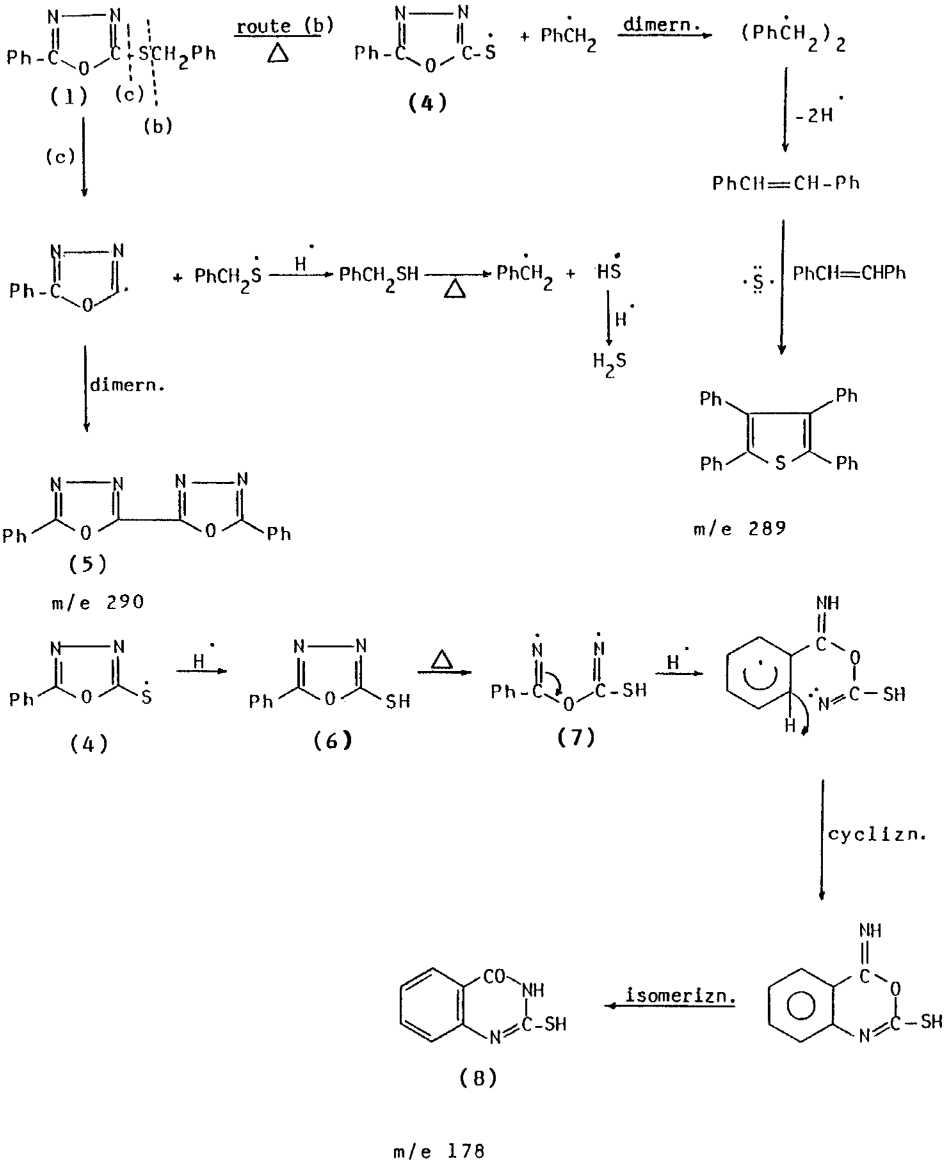
A 2-mercapto-5-phenyl-1,3,4-oxadiazolo radical (**4**) may abstract hydrogen to give 2-mercapto-5-phenyl-1,3,4-oxadiazole (**6**) which ultimately decomposes under the same reaction condition to give species **7** which may undergo intramolecular cyclization,[9] followed by isomerization,[10,11] to afford 2-mercaptoquinazolinone (**8**) as shown in Scheme 2. The structure of 8 has been established from correct analytical data, its IR spectrum that showed νNH at 3310–3340 cm^{-1}, νC=O at 1670–1690 and νSH at 2610–2630 cm^{-1}, and its electronic absorption that showed absorption maxima at 254 nm (ε33,00), 293 nm (ε16,000), 344 nm (ε22,500) and 355 nm (ε21,000) characteristic for a quinazoline moiety.[12]

Furthermore when 5-phenyl-2-mercapto-1,3,4-oxadiazole (**6**) has been heated at the same reaction condition in a separate experiment 2-mercaptoquinazolinone (**8**) has been obtained in 60% yield.

Route (c) involves homolysis of the (C—S) bond and gives rise to benzylthiyl, and 5-phenyl-1,3,4-oxadiazole radical pairs; the latter may dimerize to **5**. The



SCHEME 1

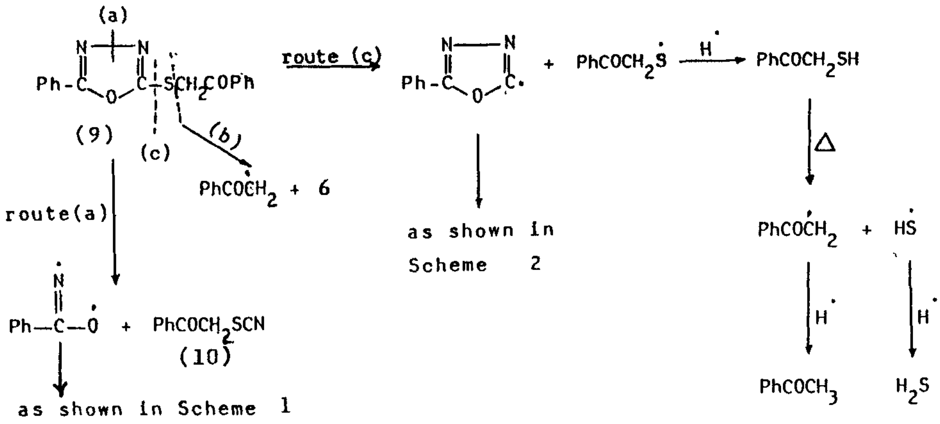


SCHEME 2

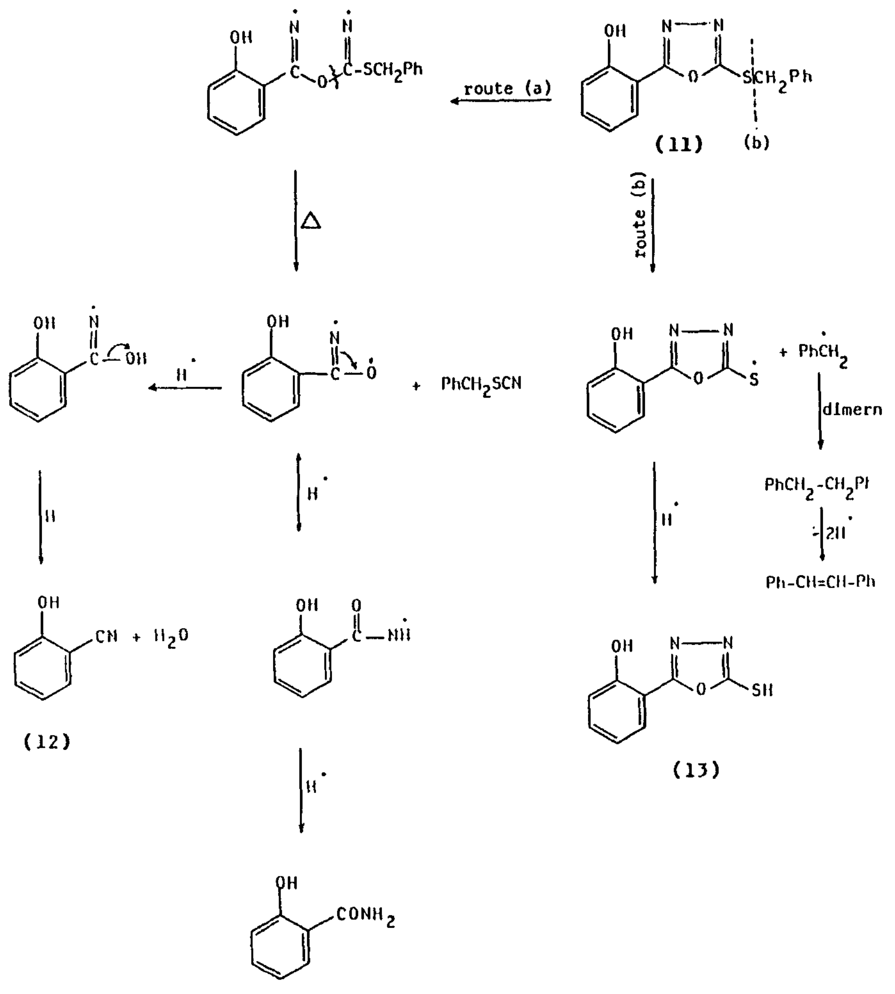
benzylthiyl radical is the precursor for benzyl mercaptan, bibenzyl, stilbene, and tetraphenylthiophene as previously discussed[13] (cf. Scheme 2).

Analogous results are obtained on pyrolysis of 5-phenyl-2-phenacylthio-1,3,4-oxadiazole (**9**) to support the generality of these rearrangement, besides formation of phenacyl thiocyanate (**10**) as shown in Scheme 3.

Attention has been given also to the thermal behaviour of 5-(2-hydroxyphenyl)-2-benzylthio-1,3,4-oxadiazole (**11**) which gives rise to bibenzyl, stilbene, benzylthiocyanate, 2-hydroxybenzamide, 2-hydroxybenzonitrile (**12**) and 5-(2-hydroxy-



SCHEME 3



SCHEME 4

phenyl)-2-mercapto-1,3,4-oxadiazole (**13**), but no 2-mercaptoquinazolinone has been detected among the products (cf. Scheme 4).

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 on glass plates covered with silica gel (0.25 mm) and eluted with acetone-petroleum ether (60–80°C)(1:9 v/v). Molecular weight determination of some reaction products was carried out by a mass spectrophotometer, Model A.E.I.M.S. 902.

5-Phenyl-2-benzylthio-1,3,4-oxadiazole (**1**) was prepared by a standard method in the literature[14]; m.p. 105° C, lit.[14] m.p. 104–7°C.

5-Phenyl-2-phenacylthio-1,3,4-oxadiazole (**9**) m.p. 147°, lit.[15] m.p. 146–148°C.

5-(2-Hydroxyphenyl)-2-benzylthio-1,3,4-oxadiazole (**11**) prepared by a standard method[15,16]; m.p. 170°C, lit.[16] m.p. 170–2°C.

General procedure. The appropriate oxadiazole derivatives (20 g of 1,9 and 11) was pyrolyzed by reflux under N_2 at 240–250°C, or in a sealed tube for 5 hr. The products were separated as indicated in a previous work.[13] 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.[13] 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.

Pyrolysis of 5-phenyl-2-mercapto-1,3,4-oxadiazole (**6**). A compound **6** (5 g) was heated in a sealed tube at *ca.* 250°C for 5 h. The pyrolysate was purified by column chromatography and gave 3 g (60%) of 2-mercaptoquinazolinone (**8**).

a) B.p. 75°C/13 mmHg; $^{n}D^{20}$ 1.5450, lit.[17] b.p. 62°C/10 mmHg, D.N.P. derivative m.p. and mm.p. 235°C.

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

c) Mixture m.p. 124°C, its I.R. spectrum coincident with that of an authentic sample.

d) M.p. 48–50°C, lit.[18] mm.p. 49–50°C.

e) M.p. 52°C. lit.[19], mm.p. 52°C, *4,4′-dinitroderivative m.p. and mm.p. 180°C of an authentic sample.*

f) M.p. 128–129°C, its I.R. spectrum identical with that of an authentic sample.

g) M.p. 42–43°C, b.p. 92–95°C/13 mmHg, lit.[20] m.p. 43°C, b.p. 256°C, its IR spectrum coincident with that of an authentic sample.

h) M.p. 19–20°C, b.p. 85°C/13 mmHg, lit.[21] m.p. 20–5°C, b.p. 83–5°C/12 mmHg; $^{n}D^{20}$ 1.5325, D.N.P. derivative m.p. and mm.p. 250°C.

i) M.p. 72–74°C, its IR spectrum coincident with that of an authentic sample. Analysis: found S 5.52; Calc. S 5.53%.

j) 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%.

k) M.p. 92–95°C, b.p. 149°C/14 mmHg, on hydrolysis gives salicyclic acid, m.p. 160°C; its IR spectrum coincident with that of an authentic sample.

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

m) M.p. 184°C, lit.[22] m.p. 185°C, analysis; Calc. S 8.71, found, S 8.26%.

n) M.p. 140–144°C, its IR spectrum coincident with that of an authentic sample.

o) M.p. 270°C, its structure is based on elemental and molecular ion determination, found N 19.30, calc. N 19.31%; M^{+} 290.

p) M.p. 212–213°C, its IR spectrum coincident with that of an authentic sample.

Preparation of reference compounds. 5-(2-Hydroxyphenyl)-1,3,4-oxadiazole-2-thiol, m.p. 212–213°C; lit.[15] m.p. 212–213°C.

2-Hydroxybenzonitrile, m.p. 92–95°C; lit.[16] m.p. 92–95°C, 5,5′-Diphenyl 2,2′-bis(1,3,4-oxadiazolyl), recrystallized from ethyl alcohol, m.p. 270°C; lit.[23] m.p. 270°C.

2-Mercaptoquinazolinone, recrystallized from acetic acid m.p. 315–316°C; lit.[24] m.p. 315–316°C.

TABLE I

Pyrolysis products of 20 g of 5-aryl-2-aralkyl thio-1,3,4-oxadiazoles.

Products in g (% of 20 g) Expt. No.	1	2	3
Carbon dioxide	evolved	evolved	-
Hydrogen sulphide	evolved	evolved	-
Water	traces	traces	traces
Benzaldehyde[a]	0.1(0.5)	-	0.8(4)
Aniline[b]	9.2(46)	1.3(6.5)	-
Stilbene[c]	0.1(0.5)	-	1.3(6.5)
Benzyl sulphide[d]	0.05(0.25)	-	-
Bibenzyl[e]	0.3(1.5)	-	1.6(8)
Benzamide[f]	0.3(1.5)	1.9(9.5)	-
Benzyl thiocyanate[g]	2.8(14)	-	2.9(14.5)
Acetophenone[h]	-	1.8(9)	-
Phenacyl thiocyanate[i]	-	1.9(9.5)	-
2-Mercaptoquinazolinone[j]	7.8(39)	8.6(43)	-
2-Hydroxybenzonitrile[k]	-	-	0.8(4)
Benzonitrile[l]	0.3(1.5)	0.8(4)	-
Tetraphenylthiophene[m]	0.2(1)	-	-
2-Hydroxybenzamide[n]	0.3(1.5)	-	0.6(3)
5,5-Diphenyl bis 2,2'-[1,3,4-oxadiazolo][o]	0.3(1.5)	1.6(8)	-
5-(2-Hydroxyphenyl)-1,3,4-oxadiazolo-2-thio[p]	-	-	0.4(2)
Residue	1.8(9)	1.4(7)	1.6(8)

Expt.(1) Pyrolysis of 5-phenyl-2-benzylthio-1,3,4-oxadiazole (**1**).
(2) Pyrolysis of 5-phenyl-2-phenacylthio-1,3,4-oxadiazole (**9**).
(3) Pyrolysis of 5-(2-hydroxyphenyl)-2-benzylthio-1,3,4-oxadiazole (**11**).

Tetraphenylthiophene m.p. 184°C; lit.[22] m.p. 185°C. 2-Hydroxybenzamide m.p. 140–143; lit.[25] m.p. 140–144°C; recrystallized from water or chloroform.

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