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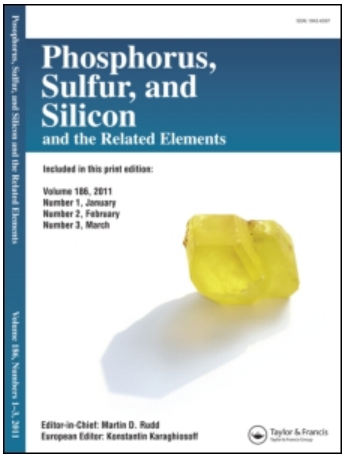

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MOLECULAR REARRANGEMENT OF SULPHUR COMPOUNDS (PART I). PYROLYSIS OF SOME SUBSTITUTED RHODANINE

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Thermal rearrangement of 3-phenylrhodanine (**I**) and 5-benzylidene-3-phenylrhodanine (**IV**) in air has been thoroughly investigated. Homolytic cleavage of (C—S) and (C—N) bonds occurred, followed by a series of hydrogen abstractions, coupling, and cyclization reactions. The isolated products of compound (**I**) are CS_2, CO, H_2S, NH_3, aniline, dibenzylamine, tribenzylamine, thioglycolic acid, phenyl isothiocyanate, bibenzyl, stilbene, *p*-aminoacetophenone, thiocarbanilide, 2-thioxoindole and 2,3,4,5-tetraphenylthiophene. In case of compound (**IV**), the isolated products are CS_2, H_2S, H_2O, CO, phenyl isothiocyanate, benzothiophene, 2-phenylquinoline, aniline, thiocarbanilide, 2-phenylindole, cinnamic acid and polystyrene. A suitable mechanism has been suggested to account for the obtained products.

Key words: Molecular rearrangement; 3-phenylrhodanine, 5-benzylidene-3-phenylrhodanine.

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INTRODUCTION

The chemistry of thiazolidinone[1-3] derivatives and their biological activities continue to attract considerable attention. Thiazolidinones are reported to exhibit antitubercular,[4] hypnotic,[5] anaesthetic,[6] antifungal,[7] anticonvulsant, antimicrobial,[8] antibacterial,[9] antiviral, insecticidal and herbicidal activity.[10-15]

On literature survey we found that the thermal rearrangement of thiazolidinone derivatives had not been investigated. We have chosen two compounds of this category and carried out their thermal rearrangement. We suggest a reasonable mechanism for these rearrangements.

RESULTS AND DISCUSSION

The work undertaken throws light on the mechanistic behaviour of pyrolysis of 3-phenylrhodanine and its benzylidene derivative.

Pyrolysis of 3-phenylrhodanine (**I**) at *ca.* 240°C for 10 hrs gives rise to the products shown in Table I. The nature of the isolated products indicated that preliminary homolytic fission of the (C—S) bond route(a) as shown in Scheme 1 occurred to give biradical ($\mathbf{I_a}$) which with further decomposition rearranged to phenyl isothiocyanate and mercaptoacetyl radical ($\mathbf{II_a}$). The latter may, upon hydrogen abstraction from the medium of the reaction, form thioglycolaldehyde, which is oxidized in air to give thioglycolic acid. The biradical ($\mathbf{I_c}$) gives rise to

TABLE I

Pyrolysis products of Rhodanines 1 and 2

Products	1	2
CS_2	Evolved	Evolved
CO	Evolved	Evolved
H_2S	Evolved	Evolved
NH_3	Evolved	—
H_2O	—	Drops
Benzylamine[a]	0.1 (0.5)	
Dibenzylamine[b]	0.3 (1.5)	
Tribenzylamine[c]	0.4 (2.0)	
Thioglycolic acid[d]	1.7 (8.5)	
Phenyl isothiocyanate[e]	1.8 (9.0)	1.8 (9.0)
Aniline[f]	2.0 (10.0)	2.5 (12.5)
Bibenzyl[g]	0.45 (2.25)	
Stilbene[h]	0.3 (1.5)	
Tretraphenylthiophene[i]	0.2 (1.0)	
2-Phenylindole[j]		0.8 (4.0)
2-Phenylquinoline[k]		0.5 (2.5)
Thiocarbanilide[l]	0.5 (2.5)	0.7 (3.5)
Cinnamic acid[m]		0.6 (3.0)
2-Thioxoindole[n]	0.2 (1.0)	
Benzothiophene[o]		0.4 (2.0)
p-Aminoacetophene[p]	0.1 (0.5)	
o-and *p*-aminophenol[q]		1.2 (6.0)
Residue	1.5 (7.5)	2.0 (10.0)

[1] Reflux of 3-phenylrhodanine in air. [2] Reflux of 3-benzylidene-5-phenylrhodanine in air.

[a] b.p. 185°C, picrate derivate m.p. and mmp. 199°C. [b] b.p. 300 dec, HCl derivative m.p. and mmp. 256°C. [c] M.p. 92°C, picrate derivative m.p. and mmp. 190°C. [d] b.p. 96°C/5 mm, n_d^{20} 1.5030. [e] b.p. 221°C, n_D^{20} 1.6515. [f] b.p. 184°C, n_D^{20} 1.5836; acetyl derivative m.p. and mmp. 113–114°C. [g] m.p. 52°C, 4,4'-dinitro derivative m.p. and mmp. 180°C of an authentic sample. [h] Mixture m.p. 124°C, I.R. spectrum identical with that of an authentic sample. [i] m.p. 184°C, I.R. spectrum identical with that of an authentic sample. [j] m.p. 188–190°C, picrate derivative m.p. and mmp. 127°C and ir spectrum are identical with that of an authentic sample. [k] m.p. 85°C, picrate derivative m.p. and mmp. 187°C. [l] m.p. 152–155°C, I.R. spectrum identical with that of an authentic sample. [m] m.p. 135°C, I.R. spectrum identical with that of an authentic sample. [n] m.p. 235°C, I.R. spectrum identical with that of an authentic sample. [o] b.p. 220°C, m.p. 30°C and I.R. spectrum identical with that of an authentic sample. [p] m.p. 108°C, I.R. spectrum identical with that of an authentic sample. [q] Separated by column chromatography silica gel (100–150) using benzene-ether (4:1) v/v as eluent, *o*-isomer (0.4 g) mmp. 174°C and *p*-isomer (0.8 g) mmp. 186°C.

2-thioxoindole[17] through sulphur extrusion[16] followed by decarbonylation and intramolecular cyclization.

Benzylamine is presumed to be formed through (N—C) bond homolysis, route (b). The biradical ($\mathbf{I_b}$) extrudes CS_2 forming biradical ($\mathbf{II_b}$).

The biradicals ($\mathbf{II_b}$) may abstract hydrogen to give acetanilide. The latter under

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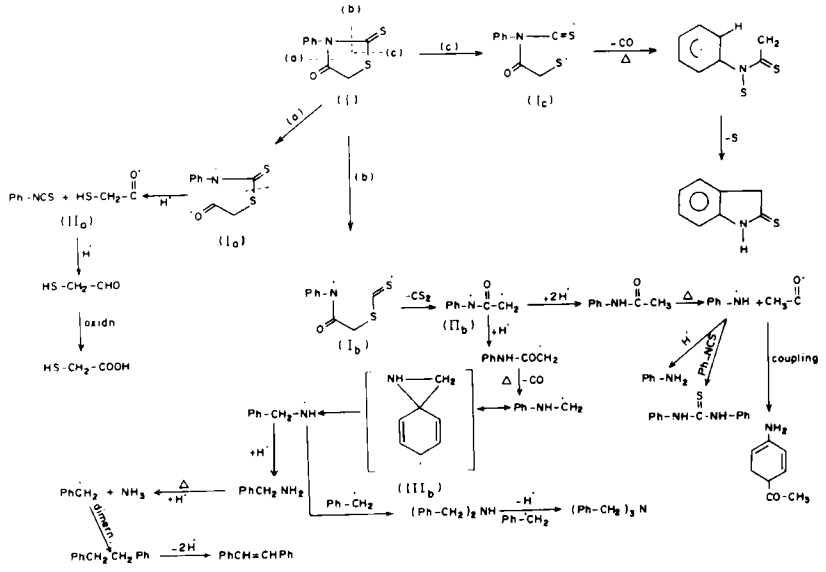


SCHEME 1

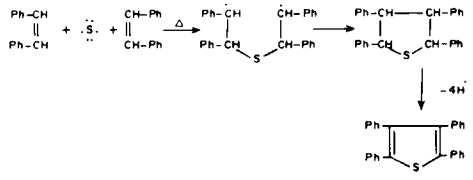
the same conditions decompose into anilino radicals and acetyl radical. The former may abstract hydrogen giving aniline or undergo coupling with acetyl radical to give *p*-aminoacetophenone.[18] The aniline so formed may couple with phenyl isothiocyanate from the medium of the reaction forming thiocarbanilide.[19]

On the other hand, the biradicals ($\mathbf{II_b}$) may undergo decarbonylation followed by H-abstraction to afford the bridged benzylaminyl radical ($\mathbf{III_b}$), then N—C phenyl migration occurs to give benzylaminyl radicals.[20]

Benzylaminyl radical can be considered as a precursor of benzylamine, dibenzylamine and tribenzylamine as reported previously.[21,22] Under the same condition, the benzylamine decomposes into benzyl radical and NH_3.[23] The benzyl radicals may undergoes dimerization forming bibenzyl followed by dehydrogenation giving stilbene.[24]

A possible pathway for the formation of tetraphenylthiophene is through dehydrogenation of tetrahydrotetraphenylthiophene formed by interaction of stilbene with sulphur, readily available in the reaction medium as reported earlier;[25] Scheme 2.

Pyrolysis of 5-benzylidene-3-phenylrhodanine (IV) under the same conditions gives rise to the products shown in Table (1).



SCHEME 2

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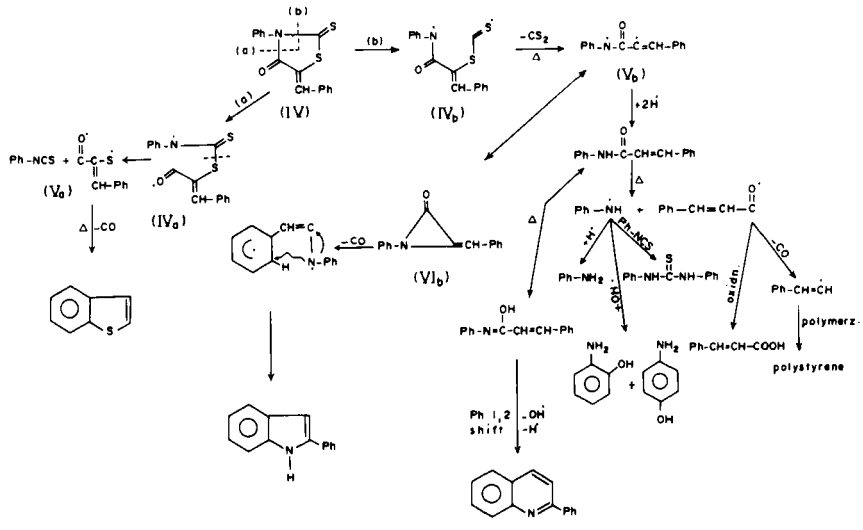

SCHEME 3

The nature of the products shows that preliminary homolysis of the (C(=O)—N) bond route (a) as shown in Scheme 3 occurred to produce biradical (**IV$_a$**) which was followed by H-abstraction and rearrangment to phenyl isothiocyanate and radical (Va). The latter upon decarbonylation forming benzothiophene.[26]

Another competing pathway for pyrolysis of 5-benzylidene-3-phenylrhodanine (**IV**) is the homolysis of the (N—C(=S)) bond route (b) leading to the formation of biradical (**IV$_b$**) may extrude CS_2 and through H-abstraction give cinnamanilide (Scheme 3).

Furthermore, pyrolysis of cinnamanilide under the same conditions was studied as shown in Table II giving anilino and cinnamoyl radical pairs. The former may abstract hydrogen forming aniline or couple with phenyl isothiocyanate to afford thiocarbanilide.

TABLE II

Pyrolysis products of cinnamanilide[a]

Products in g (%)	b.p. (°C/10 Torr)	m.p. (°C)	
Carbon monoxide			evolved
Water			drops
Aniline	60–70		2.4 (16.0)
Azobenzene[b]	155–156		1.8 (12.0)
p-Aminophenol[c]		190	0.6 (4.0)
2-Phenylquinoline		84–85	0.8 (5.3)
Cinnamic acid		133–134	2.1 (14.0)
Polystyrene[d]			4.1 (27.3)

[a] Wt. of cinnamanilide (15 g); [b] m.p. 60–62°C, its I.R. spectrum identical with that of an authentic sample; [c] m.p. 190°C, HCl derivative m.p. and mmp. 300 dec; [d] Polystyrene identified by U.V. and I.R. absorption spectra, identical with those of an authentic sample.

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O-and *p*-aminophenol presumably form through reaction of anilino radicals with hydroxyl free radicals from the reaction medium.[27]

The alternative cinnamoyl radicals may abstract hydrogen, and followed by oxidation in air, giving cinnamic acid or undergo decarboxylation and polymerization forming polystyrene.

The formation of 2-phenylquinoline proceeds through tautomerism by loss of hydroxyl free radical from the enol form of cinnamanilide.

The most probable pathway for formation of 2-phenylindole is through decarbonylation, (N—C) phenyl migration[28,29] and intramolecular cyclization of the aziridine ($\mathbf{VI_b}$) produced from biradical ($\mathbf{V_b}$).

EXPERIMENTAL

Melting points were measured with a Gallenkamp apparatus and are uncorrected. Thin-layer chromatography was carried out on glass plates covered with silica gel (25 – 40 mesh), eluting with acetone-pet. ether (60–80°C) (2:8 v/v).

Gas–liquid chromatography was carried out on Perkin–Elmer Sigma 3B. Columns used are 4ft × 4 mm, packed with 30% SE 30 on Chromosorb W (35–80 mesh), or 10% SE on Celite (60–80 mesh), using nitrogen as a carrier gas.

3-Phenylrhodanine was prepared by a standard method, m.p. 192°C, lit.[30] m.p. 190–192°C.

5-Benzylidene-3-phenylrhodanine was prepared as reported by reaction of 3-phenylrhodanine and benzaldehyde in acetic acid in the presence of sodium acetate, m.p. 186°C, lit.[31] m.p. 185°C.

Thermolysis of rhodanine derivatives: the rhodanine derivative (20 g) was heated in air at 240°C for 10 h. The gases evolved were detected by standard chemical means (NH_3 detected by Nessler's reagent), (CO detected by platinum chloride), (H_2S detected by lead acetate) and (CS_2 detected by sodium azide and iodine). The pyrolysate was subjected into its constituents by means of column chromatography over silicagel using a gradient elution technique.

The separated products were identified by physical constants; bps., mps., TLC., GLC., IR were compared with authentic samples. The results are listed in Table (I) and Table (II).

Preparation of reference compounds

2-Phenylindole, crystallized from ethanol, m.p. 188–9°C lit.[32] m.p. 188°C.
2-Phenylquinoline, m.p. 83°C, lit[33] m.p. 85°C; picrate derivative m.p. 187–8°C.
Tetraphenylthiophene, m.p. 184°C, lit.[25] m.p. 185°C. 2-Thioxoindole, m.p. 235°C, lit.[34] m.p. 237°C.

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