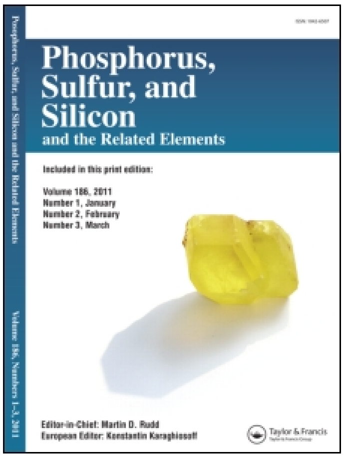

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THERMOLYSIS AND PHOTOLYSIS OF ARYL THIOCARBAMATE DERIVATIVES

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THERMOLYSIS AND PHOTOLYSIS OF ARYL THIOCARBAMATE DERIVATIVES

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Thermolysis of N-phenyl-O-phenylthiocarbamate (POPTC), N-phenyl-O-benzylthiocarbamate (POBTC), and N-phenyl-S-phenylthiocarbamate (PSPTC) by reflux for 15 hr at 220–230 °C affords degradation products assumed to be formed by homolysis at different sites furnishing free radicals that undergo subsequent reactions involving H-abstraction, dimerization, disproportionation and/or fragmentation to give the identified products. Similar results are also obtained on photolysis of such thiocarbamate derivatives.

Keywords: Thermolysis; photolysis; thiocarbamates; free radicals

INTRODUCTION

Thiocarbamates are of wide applications in industry, agriculture, and in medicine.[1] The thermal rearrangement of oxime thiocarbamates to thiooxime carbamates shows an elegant example of a 1,3-shift which was suggested to proceed through a radical mechanism.[2] However, other workers[3] suggested a cyclic reaction state where the greater nucleophilicity of sulfur, as compared with that of oxygen, provided a driving force for such rearrangement. Such controversy promoted us to investigate pyrolysis and photolysis of the title carbamates to clarify the pathway involved in rearrangement since such may lose activities or give degradation products of great importance under the effect of heat or ultraviolet irradiation. Moreover, if the carbamates are photostable, they may add to other sources of pollution in the environment.

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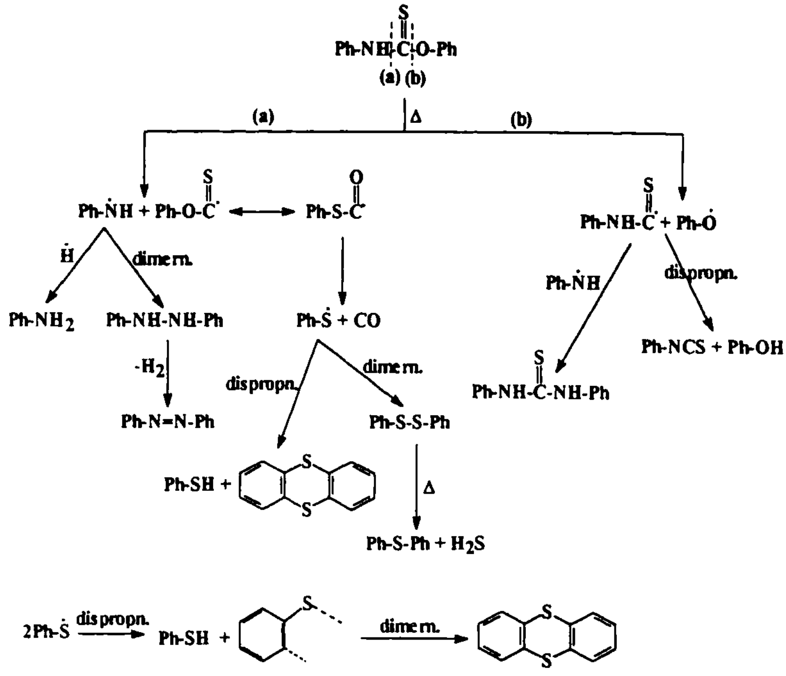
RESULTS AND DISCUSSION

The present work deals with the thermal and photodegradation of some thiocarbamate derivatives. Thermolysis of N-phenyl-O-phenylthiocarbamate (POPTC) on heating under reflux for 15 hr at 220–230 °C gave carbon monoxide, hydrogen sulfide, aniline, azobenzene, phenyl isothiocyanate, thiocarbanilide, thiophenol, diphenyl sulfide, thianthrene, and phenol. The formation of these products can be assumed to follow the series of reactions shown in Scheme 1 which implies the preliminary homolysis is the N-CS bond (route a) forming anilino and phenoxythione radical pairs. The anilino radicals may abstract hydrogen to give aniline or undergo dimerization to form hydrazobenzene which passes ultimately into azobenzene in the presence of free radicals. In contrast, the phenoxythione radical may undergo isomerization as reported earlier by other workers,[4] followed by extrusion of carbon monoxide and formation of phenylthiyl radical. Although such rearrangement is energetically unfavoured on the basis of energy values of C-C and C-S bonds being of the order of 70 and 54.5 Kcal/mol, respectively,[5] yet the extrusion of carbon monoxide provides a driving force for the rearrangement. The phenylthiyl radical may abstract hydrogen to yield thiophenol or undergo dimerization to give diphenyl disulfide which ultimately decomposes into hydrogen sulfide and diphenyl sulfide.[6]

The formation of thianthrene can be explained on the basis of the disproportionation of phenylthiyl radicals as depicted in Scheme 1. The formation of phenyl isothiocyanate, thiocarbanilide, and phenol may imply the homolysis of the OC-S bond (Route b) forming anilinothione and phenoxy radical pairs. Disproportionation of such radical pairs gives rise to phenyl isothiocyanate and phenol, whereas coupling of anilinothione radical with anilino radical gives thiocarbanilide as shown in Scheme 1.

Photolysis of POPTC in acetone for 30 hr at room temperature led to the formation of the previously separated products on thermolysis with the exception of H_2S, diphenyl sulfide, and thiantherene. The formation of these products is assumed to follow the same routes as suggested for thermolysis.

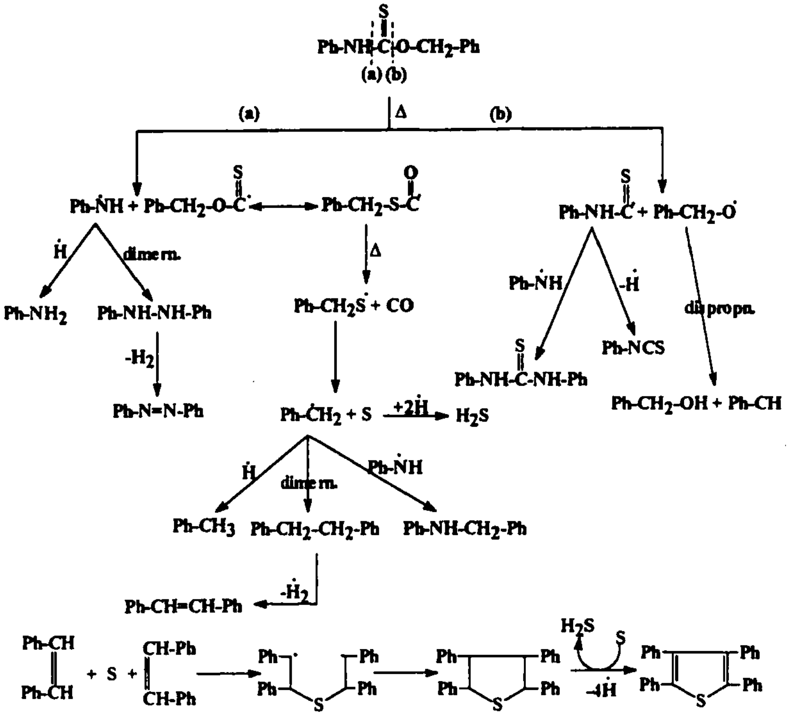
Thermolysis of N-phenyl-O-benzylthiocarbamate (POBTC) under the same conditions gave carbon monoxide, hydrogen sulfide, aniline, azobenzene, phenyl isothiocyanate, thiocarbanilide, toluene, bibenzyl, stilbene, benzyl alcohol, N-benzylaniline, and 2,3,4,5-tetraphenylthiophene as



SCHEME 1

shown in Scheme 2. The formation of these products can be explained as shown in Scheme 2 to proceed through the formation of anilino and benzyloxy thione radical pairs. The benzyloxy thione radical undergoes isomerization,[4] followed by extrusion of carbon monoxide and formation of benzylthiyl radicals. Further fragmentation of such radicals leads to formation of benzyl radicals and sulfur.[7] The normal fate of the benzyl radicals is to undergo H-abstraction and dimerization to give bibenzyl followed by dehyrogenation to produce stilbene, whereas coupling with anilino radical gives rise to N-benzylaniline.

The formation of 2,3,4,5-tetraphenylthiophene can be suggested to take place through the interaction of dibenzyl sulfide with stilbene.[8] or interaction of sulfur with stilbene.[9] However, the former mechanism was excluded on the basis of the unstability of dibenzyl sulfide under the present reaction condition, thus the sulfur suggested to be formed previously appears in the form of H_2S. Another competing pathway for thermo-



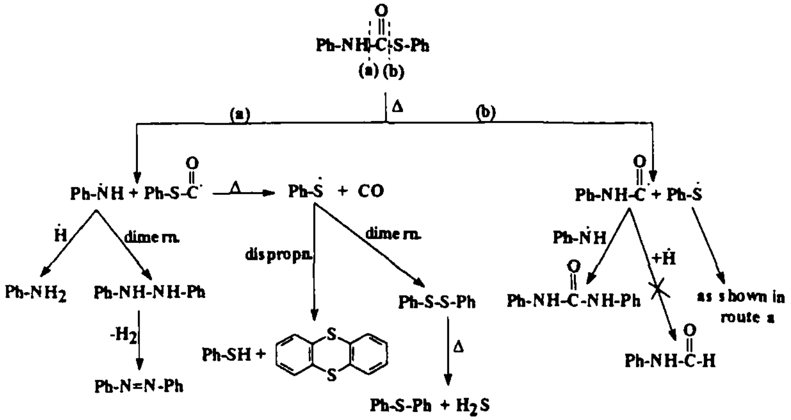
SCHEME 2

lysis of N-phenyl-O-benzylthiocarbamate is the precursor of benzaldehyde and benzyl alcohol through disproportionation of benzyloxy radicals, whereas the anilinothione radical forms phenyl isothiocyanate by loss of hydrogen or thiocarbanilide by coupling with anilino radical (Scheme 2).

Photolysis of POBTC in acetone for 70 hr at room temperature led to the formation of the previously separated products on thermolysis with the exception of azobenzene and 2,3,4,5-tetraphenylthiophene. The formation of these products was assumed to follow the same route as suggested for thermolysis.

Thermolysis of N-phenyl-S-phenylthiocarbamate (PSPTC) under the conditions used afforded carbon monoxide, hydrogen sulfide, aniline, azobenzene, phenyl isocyanate, carbanilide, thiophenol, diphenyl sulfide, and thianthrene (Scheme 3) which implied the preliminary homolysis of the N-CO bond (route a) to give anilino and thiobenzyloxy radical pairs.

The anilino radicals form aniline and azobenzene, whereas the thiobenzyloxy radical is the precursor of carbon monoxide, hydrogen sulfide, thiophenol, diphenyl sulfide, and thianthrene as shown previously in Scheme 2. In addition to, we have to take into consideration another competitive pathway (route b), although to a lesser extent as governed by the amount of carbanilide formed, whereas thermolysis leads to homolysis of the C-S bond to give phenylthiyl and phenylamidyl radical pairs. The former ones is the precursor of thiophenol, diphenyl sulfide, thianthrene, and hydrogen sulfide as discussed previously (c.f. route a), whereas the latter ones couple with anilino radical to form carbanilide (Scheme 3).



SCHEME 3

It may be suggested that the phenylamidyl radicals may abstract hydrogen to give formanilide which was found experimentally to be thermally unstable under the present reaction conditions where it undergoes decomposition into aniline, phenyl isocyanate, and water.

Moreover, the absence of formanilide among the pyrolysates indicates that the radical prefers coupling with anilino radical to form carbanilide, rather than abstracting hydrogen, due to the severe H-starvation conditions.

Photolysis of PSPTC in acetone for 15 hr at room temperature led to the formation of the previously separated products on thermolysis with the exception of H_2S, diphenyl sulfide, and thianthrene. The formation of these products was assumed to follow the same route as suggested for thermolysis.

EXPERIMENTAL

All melting points were uncorrected. The IR spectroscopic analyses were carried out on a pye-Unicam IR spectrophotometer model Sp 3–100. The GLC was carried out on Perkin-Elmer sigma 3B apparatus. Columns used 1200 m × 4 mm, packed with 30% SE 30 on Chromsorb W (35–80 mesh) or 10% SE 30 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 (25–40 mesh) and eluted with acetone-pet.ether (60–80 °C) (1:9 v/v). Molecular weight determinations of some reaction products were carried out by mass spectral analysis, Model A.E.I.M.S 902, Ultraviolet irradiation was carried using a low pressure UV lamp, Model G.L. 58, multiband UV 254/366 nm. The solutions were contained in open-topped Pyrex beakers. The solvents used were of Analar grade.

GENERAL PROCEDURE

The appropriate thiocarbamate derivatives (20 g) was heated under reflux for 15 hr. The gases evolved were detected by standard chemical means (CO_2 detected by barium hydroxide solution, CO by platinium chloride, and H2S by lead acetate). The pyrolysate was distilled under reduced pressure. Further separation of pure components from the fractions obtained was achieved by column chromatography over silica gel using a gradient elution technique. The separated products were identified by physical constants, bps, mps, TLC, GLC, and IR as compared with authentic samples whenever possible. The results are shown in Table I.

Photolysis was accomplished using a solution of the thiocarbamates (1g) in dry acetone (50 ml) irradiated at room temperature (ca. 25 °C) in the presence of trace amount of benzophenone as a sensitizer. The photolysate was separated as indicated in a previous work[10] into neutral and basic products and analyzed by GLC and compared with authentic samples using nitrobenzene as an internal standard and separated into their constituents by column chromatography over silica gel using gradient elution technique. The results are summarized in Table II.

TABLE I Thermolysis Products of Thiocarbamate Derivatives in % Yields

Products[a]	*Thiocarbamate Derivatives*		
	POPTC	*POBTC*	*PSPTC*
Thiophenol[b]	8	–	11
Diphenyl sulfide[c]	9	–	6
Thianthrene[d]	5	–	8
Aniline[e]	11	9	15
Phenyl isothiocyanate[f]	5	4	–
Thiocarbanilide[g]	16	11	–
Azobenzene[h]	3	2	5
Phenol[i]	8	–	–
Toluene[j]	5	–	–
Benzaldehyde[k]	–	11	–
Benzyl alcohol[l]	–	8	–
Bibenzyl[m]	–	5	–
Stilbene[n]	–	4	–
Tetraphenylthiophene[o]	–	6	–
N-Benzylaniline[p]	–	3	–
Carbanilide[q]	–	–	13
Unrecovered Starting	10	15	22
Residue (g)	(1.5)	(2.2)	(2.5)

a. H_2S and CO were detected by chemical means
b. identified as benzylthioether derivative, mp and mixed mp 40 °C
c. On oxidation gives diphenyl sulfone, mp and mixed mp 128 °C
d. Mp 158 C
e. bp 80–90 °C/10 Torr
f. bp110–115 °C/10 Torr,[5]
g. mp 154 °C
h. mp 62 °C
i. mp 40 °C, its benzoatederivative mp and mixed mp 70 °C
j. bp 45–50 °C/10 Torr
k. bp 70–75 °C
l. bp90–5 °C/10 Torr
m. mp 52 °C, 4,4′-dinitro derivative mp and mixed mp 180 °C
n. mp 124 °C
o. mp 184 °C, calc. S, 8.25 %; found S, 8 20 %
p. mp 38 °C, R_f=0.6
q. mp 135 °C

TABLE II Photolysis Products of Thiocarbamate Derivatives in % Yields

Products	*Thiocarbamate Derivatives*		
	POPTC	*POBTC*	*PSPTC*
Thiophenol	–	–	12
Diphenyl disulfide	8	–	11
Phenol	18	–	–
Aniline	16	18	20
Phenyl isothiocyanate	15	10	–
Thiocarbanilide	22	15	–
Azobenzene	10	–	8
Benzyl alcohol	–	12	–
Bibenzyl	–	8	–
N-Benzylaniline	–	14	–
Carbanilide	–	–	28
Unrecovered Starting	5	8	10
Residue (g)	(0.02)	(0.05)	(0.07)

Preparation of Reference compounds

N-Phenyl-O-phenylthiocarbamate (POPTC);[11] crystallized from ethanol mp 155–157 °C.

N-Phenyl-O-benzylthiocarbamate (POBTC);[12] colourless needles from ethanol mp 79–80 °C.

N-Phenyl-S-phenylthiocarbamate (PSPTC);[13] colourless crystals from ethanol mp 127–129 °C.

Diphenyl sulfide;[14] pale yellow oil bp 115 °C/3 Torr.

Thiantherene;[14] crystals from ethanol mp 156–157 °C.

Diphenyl disulfide;[15] crystallized from ethanol, mp 61 °C.

2,3,4,5-Tetraphenylthiophene;[16] colourless crystals from benzene/pet.ether (60–80 °C), mp 186–187 °C.

Benzyl isothiocyanate;[17] pale yellow oil, bp 140 °C/ 7 Torr.

sym.Diphenyl urea (carbanilide);[18] colourless crystals from glacial acetic acid, mp 240–242 °C.

References

[1] M. Z. A. Radr, M. M. Aly, S. A. Mahgoub and A. A. Atalla, *Revu. Roum. Chim.* 37, 489 (1992).

[2] B. Cross, R. J. G. Searle and R. E. Woodall, *J. Chem. Soc.*, 1833 (1971); R. F. Hudson, A. J. Lawson and E. A. C. Lucken, *Chem. Commun.* 805 (1971).

[3] H. Kwart and E. R. Evens, *J. Org. Chem.*, **31**, 410 (1966); D. H. Powers and D. S. Tartbell, *J. Am. Chem. Soc.*, **78**, 70 (1956).

[4] W. B. Ankers, C. Brown, R. F. Hudson and A. J. Lawson, *J. Chem. Soc. Chem. Commun.*, 935 (19/2).

[5] A. E. Remick "Electronic Interpretation of Organic Chemistry" J. Wiley, New York., (1949), p. 142.

[6] A. Schonberg and A. Mostafa, *J. Chem, Soc.*, 889 (1941).

[7] A. Mailhe and F. Godon, *Bull. Soc. Chim. Fr.*, **19**, 449 (1916).

[8] A. A. Abd el-Wahab and A. E. Abdel-Rahman, *Indian J. Chem.*, **20B**, 636 (1981); A. M. Gaber and M. M. Aly, *J. Anal. Appl. Pyrolysis*, **23**, 57 (1992).

[9] E. Bergman, *J. Chem. Soc.*, 505 (1930); A. E. Abdel-Rahman and A. A. Abd el-Wahab, *Indian J. Chem.*, **18B**, 402 (1979).

[10] M. M. Aly, A. M. Fahmy and A. M. Gaber, *Phosphorus, Sulfur, and Silicon*, **53**, 253 (1990).

[11] A. Rivier, *Bull. Chem. Soc. Fr.*, **35**, 840 (1901).

[12] J. Snape, *Chem. Ber.*, **18**, 2432 (1885).

[13] V. Soden and C. A. Rojahn, *Chem. Ber.*, **34**, 2309 (1901).

[14] G. Dougherty and P. D. Hammond, *J. Am. Chem. Soc.*, **57**, 117 (1935).

[15] E. Krafft and F. Vorster, *Chem. Ber.*, **26**, 2813 (1893),.

[16] E. Bergman, *J. Chem. Soc.*, 505 (1936).

[17] K. A. Hofmann, *Chem. Ber.*, **32**, 2340 (1899).

[18] A. I. Vogel "Practical Organic Chemistry" Longman, London, (1971), p. 645.