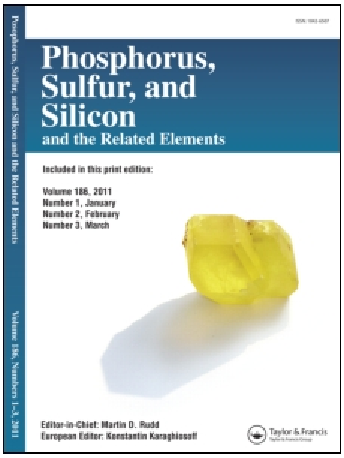

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PYROLYSIS OF ARYL DESYL SULFIDE

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PYROLYSIS OF ARYL DESYL SULFIDE†

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Phenyl desyl sulfide on pyrolysis by heating at 250°C for 15 hour, gives H_2S, benzaldehyde, benzil, bibenzyl, stilbene, thiophenol, diphenyl sulfide, thianthrene and 2,3,4,5-tetraphenylthiophene. Analogous results were also obtained on pyrolysis of *p*-tolyl desyl sulfide under the same conditions in addition to H_2O, *p*-ditolyl sulfide, thio *p*-cresol, *p*-bitolyl and 2-phenylbenzo[b]thiophene. The observed results has been interpreted in terms of a free radical mechanism involving homolysis of C—S bond.

Key words: Pyrolysis; aryl desyl sulfide.

INTRODUCTION

In continuation of our studies on photolytic and pyrolytic fragmentation mechanisms of model organic synthesis, it was reported that benzoin esters and other desyl compounds yield 2-phenylbenzofuran upon irradiation with ultraviolet light.[1,2] Thus Collier and Hill[3] have further illustrated the variability of desyl photochemistry with their report of the photolysis of compounds containing sulphur forming 2-phenylbenzo[b]thiophene was the only reported cyclization product. Recently, the importance of desyl ether derivatives in coal molecules has been stressed in order to elucidate the coal liquefaction mechanism.[4]

RESULTS AND DISCUSSION

Pyrolysis of phenyl desyl sulfide on heating at 250°C for 15 hr, gives rise to hydrogen sulfide, benzaldehyde, benzil, bibenzyl, stilbene, thiophenol, diphenyl sulfide, thianthrene and 2,3,4,5-tetraphenylthiophene (Scheme 1).

Analogous results were obtained on pyrolysis of *p*-tolyl desyl sulfide, where it gave hydrogen sulfide, water, toluene, benzaldehyde; benzil, *p*-bitolyl, *p*-bitolyl sulfide, thio *p*-cresol, bibenzyl, stilbene, 2,3,4,5-tetraphenylthiophene and 2-phenylbenzo[b]thiophene (Schemes 1 and 2).

The results point strongly to a free radical mechanism starting by homolysis of the C—S (Aryl) bond (route a) leading to the formation of aryl thiyl and desyl free radicals. The aryl thiyl radicals may abstract hydrogen from the reaction medium forming arenethiol or dimerize afford diaryl disulfide which ultimately decomposes into diaryl sulfide and hydrogen sulfide.[5] The desyl radicals may abstract hydrogen to give rise phenyl benzyl ketone, which under the same condition

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† "Desyl": Ph—CO—$\dot{C}$H—Ph.

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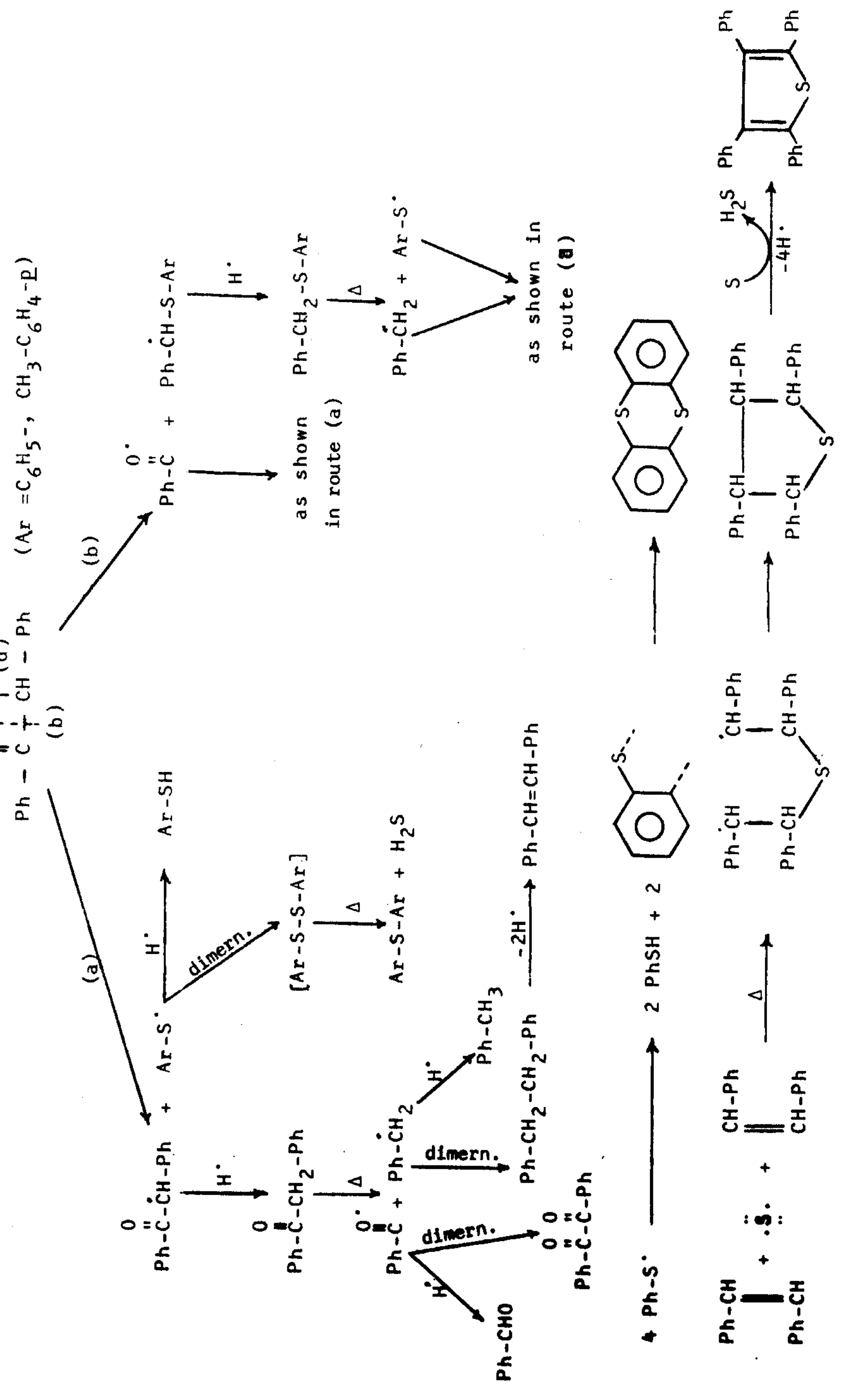
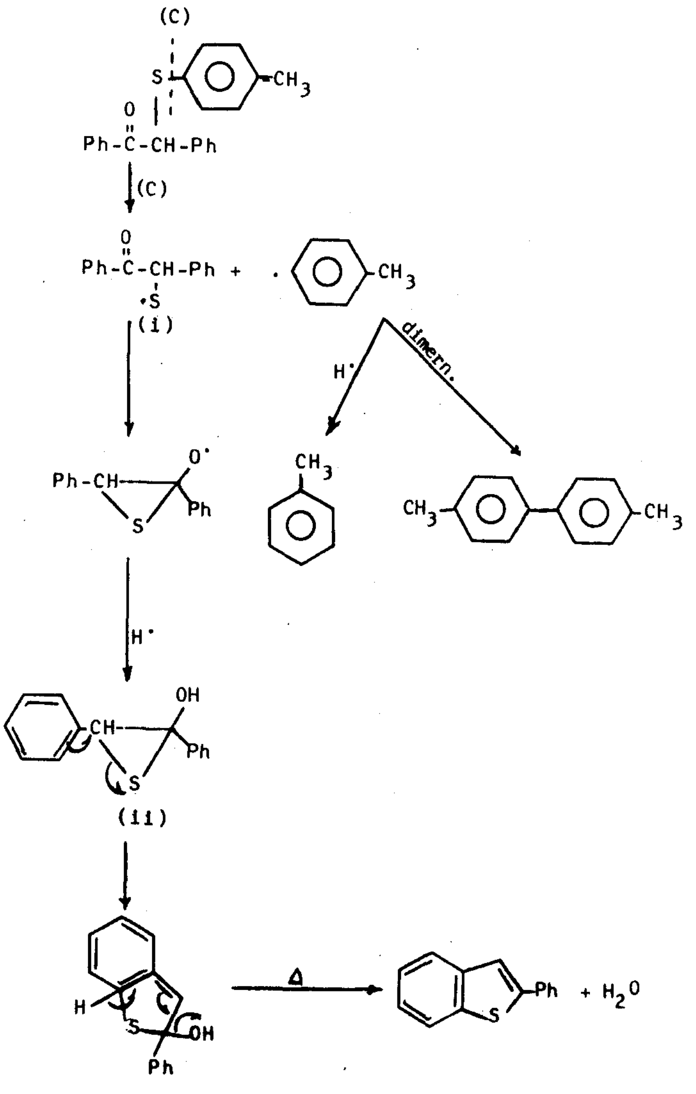

(Ar = C6H5-, CH3-C6H4-p)
(a)
(b)
(d)
dimern.
H·
Δ
-2H·
-4H·
as shown in route (a)
as shown in route (a)

(Scheme 1)



(Scheme 2)

as shown experimentally forming the benzoyl and benzyl radical pairs. The former may abstract hydrogen giving benzaldehyde or may dimerize forming benzil, whereas, the latter may undergoes dimerize to give bibenzyl which may dehydrogenated forming stilbene.[6]

A possible pathway for the formation of tetraphenylthiophene is through dehydrogenation of tetrahydrotetraphenylthiophene formed by interaction of stilbene with sulfur, readily available in the reaction medium as reported earlier[7] as (Scheme 1).

The formation of thianthrene can be explained on the basis of the disproportionation of phenyl thiyl radicals[8] as depicted in (Scheme 1).

Another competing pathway for pyrolysis of aryl desyl sulfide is the homolysis of the (C—C) bond route (b) leading to the formation of benzoyl radicals and aryl benzyl sulfide. The benzoyl radicals forming the same products as shown in route (a), whereas the pyrolysis of aryl benzyl sulfide under the same conditions gives H_2S, bibenzyl, stilbene, diaryl sulfide, thianthrene and 2,3,4,5-tetraphenylthiophene as reported earlier.[9]

Furthermore, the formation of H_2O, toluene, *p*-bitolyl and 2-phenyl-

TABLE I

Products of aryl desyl sulphide in gram (%)

	Expt. No.	
Ar	C_6H_5-	p-$CH_3C_6H_4$-
Products g(%)		
H_2S	evolved	evolved
H_2O	-	drops
Benzaldehyde[a]	2.2(14.7)	2.5(16.7)
Benzil[b]	1.6(10.7)	1.2(8)
Toluene[c]	-	2.0(13.3)
Bibenzyl[d]	1.9(12.7)	1.6(10.7)
trans-Stilbene[e]	1.5(10)	1.8(12.0)
p-Bitolyl[f]	-	1.2(8)
Diaryl sulfide	1.5(10)[g]	1.2(8)[h]
Arenethiol	1.4(9.3)[i]	1.7(11.3)[j]
Thianthrene[k]	1.7(11.3)	-
2,3,4,5- Tetraphenylthiophene[l]	1.3(8.7)	1.0(6.7)
2-Phenylbenzo[b]thiophene[m]	1.1(7.3)	-
Residue	0.6(4)	0.8(5.3)

a) B.p. 75-85°C/10 mm.Hg, estimated in the mixture as dinitro derivative m.p.230°C.

b) Mixture m.p.94°C; dinitro derivative m.p.185°C and identified by preparative tlc using pet.ether(60-80°C)/acetone (5:1 v/v) as eluent,R_f=0.85.

c) n_D^{20}: 1.4970; 2,4-dinitro derivative, m.p. and mm.p.71°C.

d) Mixture m.p. 52°C; dinitro derivative m.p. and mm.p.180°C.

e) Mixture m.p. 121°C.

f) Mixture m.p.124°C.

g) Diphenyl sulfide , B.p. 150°C/10 mm.Hg; identified as diphenyl sulfone obtained using a H_2O_2/acetic acid mixture mm.p.128°C.

h) p-Ditolyl sulfide , m.p.and mm.p.58°C and its sulfone mm.p.159°C.

i) Thiophenol, b.p.110-115°C/10 mm.Hg; n_D^{20}: 1.5880.

j) Thio p-cresol, m.p. and mm.p.42°C.

k) Mixture m.p. 158°C; m/e 216; anal.calcd. for S,29.6%;,found: 29.2%

l) Mixture m.p. 185°C; m/e 388; anal.calcd. for S, 8.25%,found: 8.00%

m) Mixture m.p. 175°C; m/e 210; anal.calcd. for S,15.24%,found: 15.04%

benzo[b]thiophene may be suggested to take place through homolysis of (C—S) bond route (C) in pyrolysis of *p*-tolyl desyl sulfide forming *p*-tolyl radicals and species (i). The former may abstract hydrogen affords toluene or may dimerize to give *p*-bitolyl[10], whereas the latter may cyclize giving episulfide (ii) with intramolecular cyclization forming water and 2-phenyl benzo[b]thiophene[3,11] as shown in (Scheme 2).

It may be noted that 2-phenylbenzo[b]thiophene was not formed as the normal product in case of pyrolysis of phenyl desyl sulfide since the resonance stabilization of the tolyl free radical enhances the homolysis of the (S—p-tolyl) bond route (C) therefore it is formed only in the case of *p*-tolyl desyl sulfide.

EXPERIMENTAL

Melting points were obtained with hot-stage apparatus calibrated with known samples and uncorrected. The IR spectroscopic analyses were carried out on a Pye-Unicam IR spectrophotometer, Model SP 8000, GLC was carried out using Perkin-Elmer Sigma 3B apparatus and the columns used are 4 ft × 4 mm packed with 30% SE 30 on chromosorb W (35–80 mesh), or 10% SE 30 on celite (60–80 mesh) at 180°C, using nitrogen as a carrier gas. TLC was carried out on glass plates covered with silica gel (100–150 mesh) and eluted with 1:4 (v/v) acetone/pet. ether (60–80°C). Molecular weight determination of some reaction products was carried out by mass spectrophotometer Model A.E.I.M.S. 902.

Phenyl desyl sulfide[12] recrystallized from ethanol, m.p. 84°C.
p-Tolyl desyl sulfide[2] recrystallized from ethanol, m.p. 79°C.

General procedure: The aryl desyl sulfide (15 g) was placed in 250 ml three-necked flask fitted with a gas inlet and a condenser. Pyrolysis was affected by heating in an oil bath at 250°C for 15 h. The gases evolved were detected by standard chemical means (H_2S by lead acetate and H_2O by anhydrous $CuSO_4$). A vigorous reaction occur accompanied by a brisk evolution of H_2S gas and the content of the flask becomes a dark brown viscous oil. A sample of the pyrolysate was analysed by glc to identify the volatile organic materials such as toluene, benzaldehyde, thiophenol. The remaining oil was separated into its constituents by means of column chromatography through silica gel using gradient elution technique and by fractional distillation under reduced pressure. The separated products were identified by a combination of elemental analysis, infrared spectra, m.p., m.m.p. with authentic samples and mass spectroscopy. The results are shown in (Table I).

Preparation of reference samples. Bibenzyl[13] crystallized from pet. ether (60–80°C), m.p. 52°C. *trans*-Stilbene[14] crystallized from ethanol, m.p. 124°C. Diphenyl sulfide[15] oil, b.p. 115°C/3 mm.Hg. *p*-Ditolyl sulfide[16] crystallized from ethanol, m.p. 129°C. Thianthrene[15] crystallized from benzene, m.p. 158°C. 2,3,4,5-Tetraphenylthiophene[17] crystallized from pet. ether (60–80°C)-benzene, m.p. 188°C. 2-Phenylbenzo[b]thiophene[18] prisms, m.p. 175°C. *p*-Ditolyl[19] crystallized from ethanol, m.p. 58°C.

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