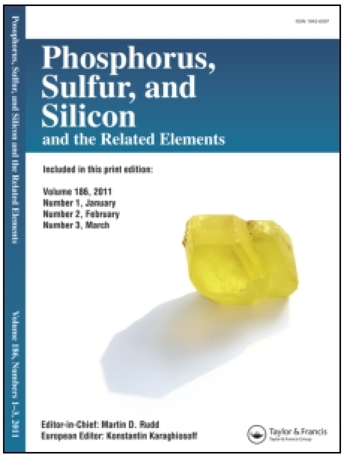

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THERMOLYSIS AND PHOTOLYSIS OF SOME SELECTED ARYL THIOESTERS

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THERMOLYSIS AND PHOTOLYSIS OF SOME SELECTED ARYL THIOESTERS

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Aryl thioesters I and II were prepared and pyrolyzed in the absence of promoters either alone or in isoquinoline as solvent. Thermolysis of β-naphthyl thiobenzoate (I) on heating in air at 250°C gives benzil, benzophenone, benzoic acid, biphenyl, thio β-naphthol, 2,2′-binaphthyl, diphenyl sulfide, thianthrene, thiophenol, phenyl β-naphthyl sulfide and 2,2′-binaphthyl sulfide. Similar results were also obtained on heating *p*-tolyl thiobenzoate (II) under the same conditions in addition to thio *p*-cresol, *p*-bitolyl, *p*-ditolyl sulfide and phenyl *p*-tolyl sulfone. H_2S and CO are also produced in all cases. Thermolysis of I and II in the presence of isoquinoline affords in addition to the above products, 1-phenylisoquinoline. Photolysis of I and II in acetone gives similar products to those of the thermolysis. From these results a free radical mechanism has been postulated to take place through the initial homolysis of C—S bond. No isomer redistribution proceeds the coupling reactions.

Key words: Thermolysis, photolysis, aryl thioesters.

INTRODUCTION

The action of Raney nickel on the decomposition of some thioesters was studied elsewhere.[1] The utility of such esters for the generation of free radicals and the possible fate of these radicals was also examined.

RESULTS AND DISCUSSION

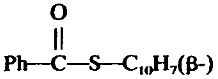
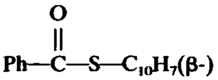
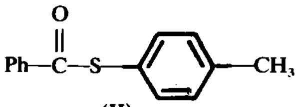
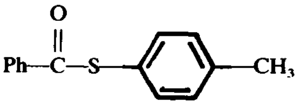
The present work deals with thermolysis and photolysis of β-naphthyl thiobenzoate (I) and *p*-tolyl thiobenzoate (II) in the absence of promoters either alone or in aromatic solvents.

β-Naphthyl thiobenzoate (I) when heated under reflux at 250°C for 20 h. underwent pyrolysis to give CO, H_2S, benzil, benzophenone, biphenyl, benzoic acid, 2,2′-binaphthyl, thiophenol, diphenyl sulfide, thio β-naphthol, thianthrene, phenyl β-naphthyl sulfide and 2,2′-binaphthyl sulfide. Similarly, *p*-tolyl thiobenzoate (II) when heated under the same conditions gives rise CO, H_2S, benzil, biphenyl, benzophenone, benzoic acid, *p*-bitolyl, thiophenol, thio *p*-cresol, *p*-ditolyl sulfide, thianthrene, diphenyl sulfide and phenyl *p*-tolyl sulfone. With isoquinoline as a solvent, the normal thermolysis of both I and II under the same conditions were accompanied by *l*-phenylisoquinoline (Table I).

The formation of the identified products strongly points to a free radical mechanism starting by the preferential homolysis of the $\overset{\overset{\displaystyle O}{\|}}{C}{-}S$ bond (route a) rather

TABLE I

Thermolysis products of thioesters (I, II) in gram (%)

Thioesters	Solvent	Neutral products	Acidic and Basic products	N R
 $\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}S{-}C_{10}H_7(\beta\text{-})}$ (I)	—	Biphenyl[a] 0.6 (4) Benzil[b] 0.8 (5.3) Benzophenone[c] 0.7 (4.7) 2,2′-Binaphthyl[d] 0.5 (3.3)	Benzoic acid[e] 1.2 (8) Thiophenol[f] 1.0 (6.7) Thio β-naphthol[g] 0.7 (4.7) Diphenyl sulfide[h] 0.8 (5.3) Phenyl-β-naphthyl sulfide[j] 1.5 (10) Thianthrene[k] 0.5 (3.3) 2,2′-Dinaphthyl sulfide[l] 1.0 (6.7)	
 $\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}S{-}C_{10}H_7(\beta\text{-})}$ (I)	Isoquinoline	Biphenyl 0.8 (5.3) Benzil 0.9 (6) Benzophenone 0.6 (4) 2,2′-Binaphthyl 0.4 (2.7)	Benzoic acid 1.5 (10) Thiophenol 1.2 (8) Thio-β-naphthol 0.8 (5.3) Diphenyl sulfide 1.0 (6.7) Phenyl-β-naphthyl sulfide 1.0 (6.7) Thianthrene 0.8 (5.3) 2,2′-Dinaphthyl sulfide 1.2 (8) *l*-Phenylisoquinoline[m] 0.6 (4)	
 (II)	—	Biphenyl 0.5 (3.3) Benzil 1.0 (6.7) Benzophenone 0.4 (2.7) *p*-Ditolyl[n] 0.6 (4)	Benzoic acid 1.0 (6.7) Thiophenol 1.0 (6.7) Thio *p*-cresol[o] 1.2 (8) Phenyl-*p*-tolyl sulfone[p] 1.1 (7.3) Diphenyl sulfide 0.9 (6) Thianthrene 0.7 (4.7) *p*-Ditolyl sulfide[q] 0.5 (3.3)	
 (II)	Isoquinoline	Biphenyl 0.7 (4.7) Benzil 0.6 (4) Benzophenone 0.5 (3.3) *p*-Ditolyl 0.4 (2.7)	Benzoic acid 1.2 (8) Thiophenol 0.8 (5.3) Thio *p*-cresol 1.0 (6.7) Diphenyl sulfide 0.8 (5.3) Thianthrene 0.9 (6) *p*-Ditolyl sulfide 0.5 (3.3) *l*-Phenylisoquinoline 0.4 (2.7)	

ture m.p. 70°C, 4,4′-dinitro derivative m.p. and mmp. 234°C.
ture m.p. 94°C; D.N.P. derivative m.p. and mmp. 185°C and identified by preparative tlc using pet. ether (60–80°C)-acetone (5:1 v/v) a
= 0.9.
ture m.p. 49°C; D.N.P. derivative m.p. and mmp. 238°C.
ture m.p. 185°C.
ture m.p. 121°C.
210°C/10 mmHg; n_D^{20}: 1.5880.
ture m.p. 81°C.
150°C/10 mmHg; and identified as diphenyl sulfone obtained from its oxidation using a H_2O_2-acetic acid mixture m.p. 128°C.
226°C/11 mmHg; mixture m.p. 50°C; its sulfone mmp. 115–116°C.
ture m.p. 158°C.
. 296°C/15 mmHg; mixture m.p. 150°C and its sulfone mmp. 176°C.
ture m.p. 95°C, picrate derivative (ethanol) mmp. 165°C.
ture m.p. 125°C.
ture m.p. 42°C.
ture m.p. 129°C.
ture m.p. 57–58°C and its sulfone mmp. 159°C.

than the $\overset{\overset{O}{\|}}{C}$—C (aryl) bond (route a)[2] forming benzoyl (III) and aryl thiyl (IV) radical pairs. The former undergoes oxidation give benzoic acid (VIII), or may dimerize to give benzil (VI), whereas the latter may couple with aryl radical from the medium of the reaction forming diaryl sulfide (VII).

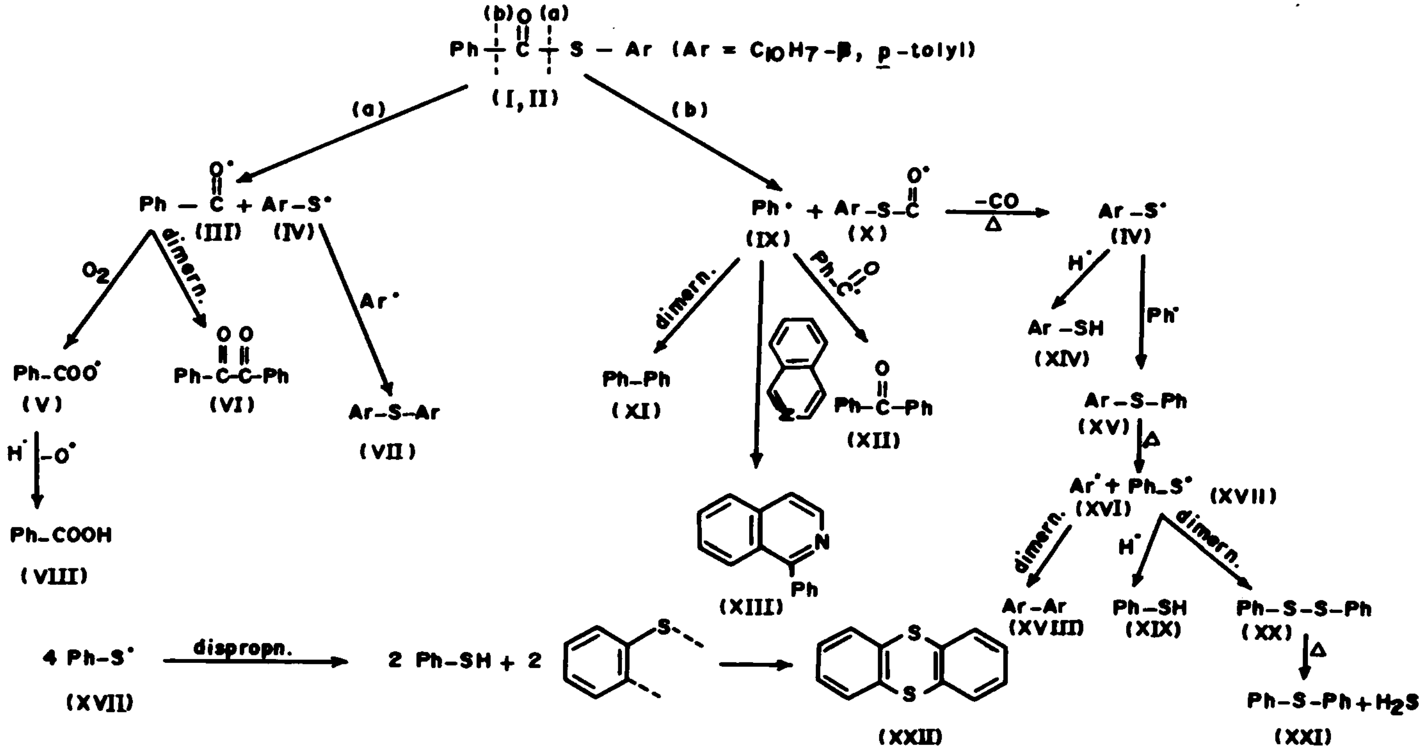
On the other hand, the probability of the homolysis of $\overset{\overset{O}{\|}}{C}$—C (aryl) bond (route b) into phenyl radical (IX) and aryl sulfoyl (X) radical. The phenyl radicals may dimerize to give biphenyl (XI) or may couple with benzoyl radical affords benzophenone (XII) and with isoquinoline as a radical scavanger forming *l*-phenylisoquinoline (XIII) whereas, the aryl sulfoyl radicals undergo subsequently decarbonylation leads to the formation of aryl thiyl radicals which may abstract hydrogen to give thioaryl (XIV) or couple with phenyl radical forming phenyl aryl sulfide (XV) which under the same conditions decompose[3] at 250°C for 20 h. affords aryl radical (XVI) and phenyl thiyl radicals (XVII). The aryl radical may dimerize forming biaryl[4] (XVIII) but the phenyl thiyl radicals may abstract hydrogen giving thiophenol (XIX) or undergo dimerize affords diphenyl disulfide (XX) which ultimately decomposes into hydrogen sulfide and diphenyl sulfide[5] (XXI) as shown in (Scheme 1).

The formation of thianthrene (XXII) can be explained on the basis of the disproportionation of phenyl thiyl radical[6] as depicted in (Scheme 1).

Photolysis of both I and II in acetone solution at 25°C for 30 h. affords analogous products to those on thermolysis with the exception of diaryl sulfide and the photodegradation products of phenyl aryl sulfide; namely H_2S, thiophenol, biaryl, diphenyl sulfide and thianthrene. A result which indicates its photostability under the given conditions as shown experimentally. Hence, it can be concluded that photolysis follows the same routes as thermolysis to give radicals which either react within the solvent cage or escape out of the cage, followed by the usual free radical reactions involving H-abstraction, dimerization and coupling as discussed previously.

EXPERIMENTAL

All melting points are uncorrected. The IR spectroscopic analysis were carried out on a Pye-Unicam IR spectrophotometer Model Sp. 200 G. GLC was carried out using Perkin-Elmer Sigma-3B apparatus and the columns used are 4ft x 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 a carrier gas. Thin-layer chromatography was carried out on glass plates covered with silicagel (25–40 mesh) and eluted with acetone-pet. ether (60–80°C) (1:4 v/v). Molecular weight determination of some reaction products was carried out by mass spectrophotometer. Model A.E.I.M.S. 902. Ultraviolet irradiation was carried out using Mallinkrodt 150 W mercury discharge lamp and the solutions were contained in open topped pyrex beakers. The solvents used were analar grade and used without further purifications. All experiments were carried out in duplicate.


(b) O (a)
Ph–C–S – Ar (Ar = C10H7-β, p-tolyl)
(I,II)
(a)
(b)
Ph — C(=O•) + Ar–S•
(III)
(IV)
O2
dimern.
Ar•
Ph–COO•
(V)
Ph–C–C–Ph
(VI)
Ar–S–Ar
(VII)
H• –O•
Ph–COOH
(VIII)
Ph• + Ar–S–C(=O•)
(IX)
(X)
–CO
Δ
Ar–S•
(IV)
dimern.
Ph–C=O
Ph–Ph
(XI)
Ph–C(=O)–Ph
(XII)
N
Ph
(XIII)
H•
Ph•
Ar–SH
(XIV)
Ar–S–Ph
(XV)
Δ
Ar• + Ph–S•
(XVI)
(XVII)
dimern.
H•
dimern.
Ar–Ar
(XVIII)
Ph–SH
(XIX)
Ph–S–S–Ph
(XX)
Δ
Ph–S–Ph + H2S
(XXI)
4 Ph–S•
(XVII)
dispropn.
2 Ph–SH + 2
S
S
S
(XXII)

Scheme I

TABLE II

Photolysis products of aryl thioesters (**I** and **II**) in gram (%)

Products in gram (%)	I	II
H_2S	—	—
CO	detected	detected
Benzil	0.13 (13)	0.1 (10)
Benzoic acid	0.25 (25)	0.21 (21)
Biphenyl	0.16 (16)	0.08 (8)
Benzophenone	0.08 (8)	0.11 (11)
Thio-β-naphthol	0.1 (10)	—
Thio-*p*-cresol	—	0.15 (15)
Phenyl β-naphthyl sulfide	0.2 (20)	—
Phenyl *p*-tolyl sulfone	—	0.23 (23)
Residue	0.08 (8)	0.14 (14)

β-Naphthyl thiobenzoate[7]: Crystallized from ethanol as white crystals, b.p. 267°C/15 mm.Hg., m.p. 108°C.

p-Tolyl thiobenzoate[8]: Crystallized from ethanol as white crystals, m.p. 75°C.

Thermolysis of thioesters derivatives. The thioesters (15 g) were heated on an oil bath (bath temp. 250°C) for 20 h. either alone (Experiments 1, 2) or in 15 ml isoquinoline as solvent (Experiments 3, 4). The gases evolved were detected by standard chemical means (CO by platinum chloride test paper and absorbed in a trap containing ammonical cuprous chloride and H_2S by lead acetate). The products were separated into neutral, basic and acidic components as described in a previous work.[9] The separated products were subjected to further separation into their constituents by means of column chromatography over silicagel using gradient elution technique and by fractional distillation under reduced pressure and identified by TLC and GLC or by comparison of their infrared spectra with those of authentic samples. The results are given in Table 1.

Photolysis of aryl thioesters. A solution of thioesters (1 g) in dry acetone (50 ml) was irradiated at room temperature (25°C) for 30 h. The photolysate was separated as indicated in a previous work[10] into neutral and acidic products and analyzed by GLC as compared with authentic samples using nitrobenzene as internal standard and separated into their constituents by column chromatography. The results are summarized in Table II.

Preparation of references samples

1. 2,2′-Binaphthyl[11]: crystallized from ethanol, m.p. 185°C.
2. Phenyl β-naphthyl sulfide[12]: crystallized from ethanol, m.p. 52°C.
3. Diphenyl sulfide[13]: oily b.p. 115°C/3 mm.Hg.
4. Thianthrene[13]: crystallized from benzene, m.p. 158°C.
5. 2,2′-Dinaphthyl sulfide[7]: crystallized from ethanol, m.p. 151°C.
6. *l*-Phenylisoquinoline[14]: crystallized from pet. ether (60–80°C), m.p. 96°C.
7. *p*-Ditolyl[15]: crystallized from ethanol, m.p. 125°C.
8. Phenyl *p*-tolyl sulfone[16]: crystallized from ethanol, m.p. 129°C.
9. *p*-Ditolyl sulfide[17]: crystallized from ethanol, m.p. 58°C.

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