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THERMAL FRAGMENTATION AND REARRANGEMENT OF β -KETOSULFIDE AND β -KETOSULFONE DERIVATIVES

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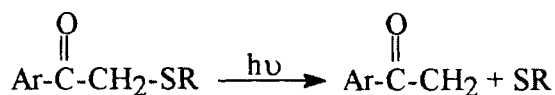
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Thermal fragmentation and rearrangement of neat phenacyl aryl sulfides **I** and **II** have been thoroughly investigated and found to involve cleavage of the C-S and C-C bonds followed by a series of H-abstraction, coupling, dimerization, rearrangement, and cyclization reactions. Also, in the presence of isoquinoline as a radical trap, **I** gave 1-phenyl- and 1-benzylisoquinoline in addition to the rearrangement products. Analogous results, beside SO₂ arylsulfonic acid and biaryl, were also obtained on heating phenacyl aryl sulfones **III** and **IV** in tetraline. A suitable mechanism has been suggested to account for the isolated products.

Keywords: Thermal Fragmentation; Rearrangement; β -Ketosulfides and sulfones; Free radicals

INTRODUCTION

Photochemical behavior of carbonyl compounds containing γ -halogens has been documented.^[1] It has been reported that photolysis of ω -ethylthioacetophenone^[2] involves abstraction of a γ -halogen atom producing a diradical intermediate, which either undergoes cleavage and/or a radical combination to cyclobutanol derivatives.^[3] Wagner et al.^[4] have reported that photochemistry of β -, γ -, δ -phenacyl sulfides, sulfoxides, and sulfones which undergo type II photo elimination and no irreversible reaction. The same authors studied^[5] the quantitative effect of ring- and α -substituents as well as sulfur oxidation state of the cleavage:





RESULTS AND DISCUSSION

In the present work, the thermolysis of phenacyl phenyl sulfide **I** via reflux at 240–260°C for 20 hr could be interpreted to proceed through a rearrangement mechanism involving the two competing C-S and C-C bonds fission pathways which resulted in the formation of CO, H₂S, benzene, biphenyl, benzil, acetophenone, bibenzyl, stilbene, diphenyl sulfide, thianthrene, 2,3,4,5-tetraphenylthiophene, and 2-phenylbenzo[b]-thiophene as shown in Scheme 1.

The formation of the isolated products strongly points to a free radical mechanism starting by the preferential homolysis of the C-S bond (route a) rather than C-C bond (route b)^[7] forming phenacyl and phenylthiyl radicals pairs. The phenacyl radical may abstract hydrogen to give acetophenone whereas, the phenylthiyl may abstract hydrogen to form thiophenol or undergo dimerization to form diphenyldisulfide which ultimately decomposes under the present conditions to give H₂S and diphenyl sulfide.^[8] The formation of thianthrene can be explained on the basis of disproportionation of phenylthiyl radical^[9] as depicted in Scheme 1.

Another competing pathway in the thermal rearrangement of **I** is the homolysis of the C-C bond (route b) into benzoyl and phenylthiomethyl radical pairs. The benzoyl radical is the precursor of biphenyl and benzil through decarbonylation and dimerization processes, respectively.^[10] The phenylthiomethyl radical may undergo sulfur rearrangement through a 1,2-phenyl shift via a 3-centered bridged radical intermediate,^[11] in a manner similar to that reported for phenoxymethyl radical,^[11] to give benzyl radical and sulfur molecule. The benzyl radical can be considered as the precursor of bibenzyl and stilbene through dimerization followed by dehydrogenation. The formation of 2,3,4,5-tetraphenylthiophene takes place through the interaction of stilbene with sulfur which is readily available in the reaction medium as reported earlier.^[12]

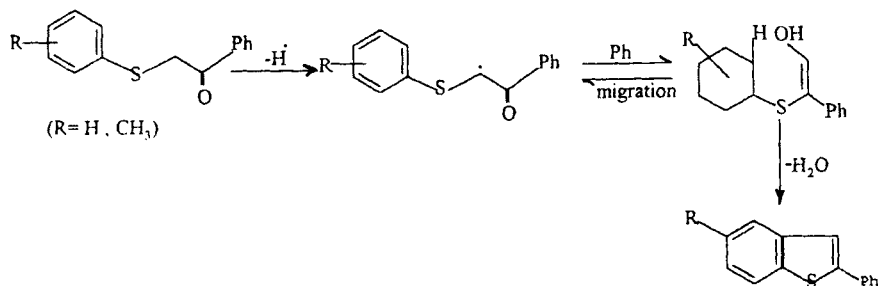
Moreover, phenacyl radicals undergo rearrangement through a 1,2-shift of a phenyl group, analogous to neophyl radical,^[13] to give benzyl radical and carbon monoxide. The normal fate of benzyl radical was discussed as shown previously (Scheme 1, route b).

A possible pathway for the formation of 2-phenylbenzo[b]thiophene is through H-abstraction of compound **I**, then tautomerize into the enol form followed by intramolecular cyclization.^[14a,b] Moreover, the formation 2-phenylbenzo[b]thiophene from stilbene and sulfur is also possible.

Furthermore, the formation of benzothiophene derivatives confirm that phenacyl aryl sulfides **I** and **II** act as good H-donors in the reaction medium (Scheme 2).

Analogous results were also obtained in the thermal fragmentation of phenacyl *p*-tolyl sulfide **II** which gave rise to CO, H₂S, biphenyl, acetophenone, bibenzyl, stilbene, benzil, *p*-thiocresol, di-*p*-tolyl sulfide, bitolyl, and 5-methyl-2-phenylbenzo[b]thiophene. Such products can be interpreted with the same mechanism suggested previously in Schemes 1 and 2.

The formation of *p*-thiocresol, *p,p*-bitolyl and di-*p*-tolyl sulfide was explained through dimerization of *p*-tolylthiyl radical to give *p,p*-ditolyldisulfide which decomposes into *p*-thiocresol, *p*-bitolyl,^[15] and di-*p*-tolyl sulfide^[16] (Scheme 1).



SCHEME 2

Similarly, thermal rearrangement of phenacyl phenyl sulfide **I** in the presence of isoquinoline as a radical trap under the used condition gave 1-phenyl- and 1-benzylisoquinolines, in addition to the previous products (Scheme 1 and Table I). Trapping of phenyl and benzyl radicals by isoquinoline as a radical scavenger may be considered as further evidence for free radical reactions. However, no isomer redistribution takes place in the coupling reactions. This is because recombination of radicals is faster than either position isomerization or radical transfer reactions.^[17]

Phenacyl aryl sulfones **III** and **IV**, on thermolysis in boiling anhydrous tetraline (ca. 210°C) for 2 h, leads to the formation of CO, SO₂, benzil, biaryl, acetophenone, stilbene, bibenzyl, diaryl sulfide, arenethiol, arene, diaryl sulfone, and arenesulfonic acid as shown in Schemes 3 and 4.

The formation of these products can be assumed to follow the series of reactions which imply the preliminary homolysis C-S bond (route a) forming phenacyl and arenesulfonyl radical pairs. The normal fate of phenacyl radicals was discussed as mentioned before (Scheme 1).

Some of arenesulfonyl radicals undergo desulfonylation, forming aryl free radicals which dimerize to the corresponding biaryl (Scheme 3). Dimerization of arenesulfonyl free radicals through S-S coupling leads to the formation of the corresponding diaryl sulfone (Scheme 4, Eq. 1). The low yield of diaryl sulfones gives a clue for their instability, especially in the case of di-*p*-tolyl sulfone.^[18]

On similar grounds, sulfinyl sulfonates that may be formed from dimerization through S-O coupling are unlikely to be formed or, even if they are formed, they will readily dissociate into sulfinyl and sulfonate radical pairs and the whole process appears as one disproportionation process (Eq. 2, Scheme 4).

The coupling of a sulfonyl radical with a sulfonate radical would give sulfonic anhydride which easily undergoes hydrolysis during working-up procedure to

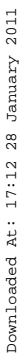
Table 1. Thermal Rearrangement Products of Phenacyl Aryl Sulfide I and II in % yield

Entry	Sulfides	Conditions ^a			Neutral Products %		Thiols and Basic products %		Neutral Residue (g)
		Solvent	Temp. °C	Time, h					
1	$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{S}-\text{Ph}$ <p style="text-align: center;">I</p>	-	240	20	Benzene ^b	10	Thiophenol ^c	6	1.4
					Biphenyl	7			
					Benzil	4			
					Acetophenone ^d	8			
					bibenzyl	6			
					Stilbene	10			
					Diphenyl sulfide	11			
					TPT	14			
					Thianthrene	8			
					2-Phenylbenz-[b]thiophene ^e	12			
2	$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{S}-p\text{-tolyl}$ <p style="text-align: center;">II</p>	-	240	8	Benzene	14	Thiop-cresol ^h	8	1.7
					Biphenyl	9			
					Benzil	6			
					Acetophenone	11			
					Bibenzyl	5			
					Stilbene	8			
					p,p-Bitolyl ^g	10			
					p,p-Ditolyl sulfide ^f	11			
					5-Methyl-2-Phenylbenzo[b]thiophene ^g	15			
3	$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{S}-\text{Ph}$ <p style="text-align: center;">I</p>	Isoquinoline	260	20	Benzene	12	Thiophenol	8	1.3
					Biphenyl	6			
					Benzil	5			
					Acetophenone	10			
					Stilbene	9			
					Diphenyl sulfide	10			
					TPT	10			
					Thianthrene	7			
					2-Phenylbenz-[b]thiophene	8			

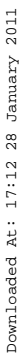
^a The conversion was completed at the end of thermolysis, ^b determined by gic analysis of the crude pyrolysate; ^c collected at 165-170 °C and was identified as the benzyl thioether derivative, m.p. 41 °C, which upon oxidation with CrO₃ / acetic acid gave benzyl phenyl sulfone, m.p. and mm.p. 148 °C (lit.³³ m.p. 148 °C); ^d collected at 65-70 °C / 3 Torr, 2,4-dinitro derivative, m.p. and mixed m.p. 250 °C; ^e crystallized from ethanol, m.p. 125 °C (lit.³⁴ m.p. and mm.p. 124-6 °C); ^f ¹H NMR δ 7.2 (m, 4 H), 7.4-7.5 (m, 4 H), 2.3-2.4 (s, 6 H); ^f crystallized from ethanol, m.p. 58 °C (lit.³⁵ m.p. and mm.p. 59-60 °C); ^g crystallized from ethanol, m.p. 157 °C (lit.^{14a} m.p. 158 °C), found: C, 80.3, H, 5.4; S, 14.1%. Calcd. for C₁₅H₁₂S, C, 80.36, H, 5.37; S, 14.2%; ^h collected at 60-65 °C / 3 Torr, m.p. and mm.p. 40-2 °C; ¹H NMR δ 7.2 (m, 2 H), 7.4 (m, 2 H), 2.3 (s, 3 H), 3.4 (s, 1 H); ⁱ collected at 75-82 °C / 8 Torr, ²⁰ND : 1.6051; picrate derivative, m.p. and mm.p. 219-221 °C.

give the corresponding sulfonic acid^[19] (Scheme 4, Eq. 3). The coupling of arenesulfinyl radical with an anenesulfonyl radical was reported^[20] to give thio-sulfonate that subsequently tends to decompose thermally forming ultimately thiophenol, diaryldisulfide, and arenesulfonic acid (Eqs. 4 and 5). Heating of diaryldisulfide under the same conditions gave diaryl sulfide and H₂S.^[8]

Desulfonylation of some arenesulfonyl radicals could account for the liberation of sulfur dioxide and the formation of aryl radicals which may then, in



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other successive reactions (Scheme 4, Eq. 6–Eq. 10), form the corresponding biaryl by dimerization, arene by H-abstraction or diaryl sulfide by coupling with arylthiyl radical as shown in Schemes 3, 4.

In naphthalene, the normal thermolytic products of the phenacyl phenyl sulfone **III** under the conditions used were obtained together with isomeric, 1- and 2-benzyl naphthalene (yield, 32.2 %) were produced in the ratio of (70.3% 1- to 27.2% 2-isomer).

Absence of isomeric 1- and 2-phenyl naphthalene and binaphthyl from the thermolysis mixture confirms the assumption that a radical substitution process takes place to give benzylation products.

EXPERIMENTAL

All melting points were determined on a Kofler melting point apparatus and were uncorrected. IR spectroscopic analyses were carried out on a Pye-Unicam SP 3-100. Thin layer chromatography was performed using 10 × 3 cm glass plates coated with silica gel and/or ready made and eluted 10% ether-pentane. column chromatographic separations were carried out using 100 × 2.5 cm glass column packed with Kieselgel 60 (0.040–0.063 mm) using successively solvents: pet. ether (40–60°C); pet. ether (40–60°C)-pet. ether (60–80°C) mixtures; pet. ether (60–80°C); pet. ether (60–80°C)-benzene mixtures; benzene; benzene-ether mixtures; and finally ether. gas liquid chromatography was carried out on a Perkin-Elmer model Sigma 3B apparatus; the column used was (8 × 1/8 cm) packed with 30% SE 30 on Chromosorb W(35–80 mesh), using nitrogen as a carrier gas. GC-MS analyses were carried out using Finnigan Mat EI-SSQ 7000 apparatus and ¹H NMR spectra for starting materials and some reaction products were recorded using a Varian EM 270 MHz instrument at MPI für Strahlenchemie in Mülheim, Germany.

Starting Materials

Phenacyl phenyl sulfide **I**, b.p. 173–177°C, crystallized from ethanol, m.p. 50°C (lit,^[21] m.p. 49–50°C), ¹H NMR δ 4.2 (s, 2 H), 7.2 (m, 8 H), 7.8 (m, 2 H); *m/z* 228.

Phenacyl *p*-tolyl sulfide **II**, b.p. 184–188°C, crystallized from ethanol, m.p. 35°C (lit,^[22] m.p. 36–37°C), ¹H NMR δ 2.3 (s, 3 H), 4.1 (s, 2 H), 7.1 (m, 8 H), 7.6 (d, 2 H); *m/z* 242.

Phenacyl phenyl sulfone **III**, crystallized from ethanol, m.p. 95°C (lit,^[23] m.p. 96–97°C), ¹H NMR δ 1.4–3.8 (s, 2 H), 7.2 (m, 8 H), 7.8 (m, 2 H); *m/z* 260.

Phenacyl *p*-tolyl sulfone **IV**, crystallized from ethanol, m.p. 110°C (lit.^[23] m.p. 110–112°C), ¹H NMR δ 1.2–2.0 (s, 3 H), 2.4–3.4 (s, 2 H), 7.0 (m, 8 H), 7.4 (d, 2 H); m/z 274.

It is worthwhile to mention that a number of preliminary experiments were carried out to determine the proper temperature for thermolysis. However, the results showed that the decomposition of **I** and **II** starts above 240°C and above 200°C for **III** and **IV**. Also, it was found that these temperatures are the lowest at which the conversion of the sulfides **I** and **II** and the sulfones **III** and **IV** was completed.

Thermal Fragmentation of Phenacyl Aryl Sulfides **I** and **II**, General Procedure

The sulfide (0.043 mol) was placed in a 50 ml, round bottom flask fitted with an efficient reflux condenser (1.5 m length) and heated either alone (Expts. 1 and 2) or in 5 ml of isoquinoline solvent (Expt. 3) using a temperature controlled heating mantle adjusted to the desired temperature. The temperature was measured using a thermometer immersed in the reaction flask. The exit gases were trapped in lead acetate solution (for H₂S) and passed over palladium chloride for CO. After decomposition was complete, the pyrolysate was subjected to normal distillation up to 180°C, using a microdistillation system, for separation of low boiling products such as benzene and toluene. Benzene was collected at 70–80°C and its glc analysis showed a single peak at 0.7 min at 90°C, as for an authentic sample. Toluene was collected at 105–110°C and revealed a single peak at 1.0 min at 90°C, comparable with an authentic sample. Fractional distillation under reduced pressure gave acetophenone, diaryl sulfide, isoquinoline, and arenethiols (Expts 1–3).

The nondistillable residue was dissolved in ether, and the ether solution was extracted with two 10-ml portions of 5% NaOH solution for the separation of the thiols. The alkaline extracts were separately neutralized with 2 *M* HCl, and the thiols were separated and identified either directly by glc and/or column chromatography (Expts. 1–3) or separated into neutral and basic products (Expt. 3) using HCl solution. In Expt. 1, the tetraphenylthiophene (TPT) was separated by filtration as an ether insoluble product and recrystallized from amyl alcohol, m.p. and mm.p. 189°C (lit.^[24] m.p. 185°C). The ether soluble neutral products were eluted from chromatography column using the former sequence of eluents. Biphenyl was eluted with pet. ether (40–60°C), and showed a glc peak at 3.0 min at 140°C, m.p. and mm.p. 70°C. Bibenzyl was eluted with pet. ether (40–60°C)-pet. ether (60–80°C) mixtures (1:2, v/v), and showed a glc peak at 3.3 min at 140°C, m.p. and mm.p. 52°C (lit.^[25] m.p. 52–53°C); ¹H NMR δ 7.2–7.4

(m, 5 H), 7.3–7.4 (m, 5 H), 2.8 (s, 4 H). Stilbene was eluted with pet. ether (60–80°C), m.p. and mm.p. 125°C (lit.,^[26] m.p. 124°C). Diphenyl sulfide was eluted with pet. ether (60–80°C)-benzene (1:1, v/v) and identified as diphenyl sulfone obtained from its oxidation using H₂O₂-acetic acid mixture,^[27] m.p. and mm.p. 128°C (lit.,^[28] m.p. 128–129°C). Thianthrene was eluted with pet. ether (60–80°C)-benzene (5:1, v/v), m.p. and mm.p. 158°C (lit.,^[29] m.p. 158–159°C); ¹H NMR δ 7.2 (m, 4 H), 7.4–7.5 (m, 4 H). 2,3,4,5-Tetraphenylthiophene (TPT), in part, was eluted with pet. ether (60–80°C)-benzene (1:1, v/v), m.p. and mm.p. 188°C (lit.,^[24] m.p. 185°C); calcd. S: 8.25; found S: 8.26%; *m/z* 388. Benzil was eluted with pet. ether (60–80°C)-benzene (1:2 v/v), m.p. and mm.p. 96°C. 2-Phenylbenz[b]thiophene was eluted with benzene-ether (1:1, v/v), m.p. and mm.p. 175°C (lit.,^[30] m.p. 174–175°C); ¹H NMR δ 7.4 (m, 2 H), 7.5 (m, 2 H), 8.1–8.2 (m, 5 H), 2.1 (s, 1 H); found : C, 80.2; H, 4.8; S, 15.0. Calcd. for C₁₄H₁₀S : C, 80.0; H, 4.8; S, 15.2%; *m/z* 210.

The amine fraction was extracted with ether (Expt. 3). Ether was evaporated and recovered isoquinoline was collected at 75–82°C/5 Torr. The residue was analyzed using column chromatography. 1-Phenyliso-quinoline (Expt. 3) was eluted with pet. ether (60–80°C)-benzene (2:3, v/v), m.p. and mm.p. 95°C (lit.,^[31] m.p. 95–96°C); picrates m.p. 164°C (ethanol) (lit.,^[31] m.p. 165–166°C). 1-Benzylisoquinoline (Expt. 3) was eluted with pet. ether (60–80°C)-benzene (1:1, v/v), m.p. and mm.p. 55°C (lit.,^[32] m.p. 56°C); picrates m.p. 180°C (ethanol) (lit.,^[31] m.p. 182°C). Moreover, in Expt. 3, the mixture of 1-benzyl- and 1-phenyliso-quinolines was analyzed using preparative thin layer chromatography, *R_f* = 0.4 and 0.6, respectively, and the eluent used was a pet. ether (60–80°C)-benzene mixture (1:1, v/v).

Thermal Fragmentation of Phenacyl Aryl Sulfones III and IV

The appropriate sulfone (0.038 mol) was placed in 100-ml, three-necked flask fitted with a gas inlet and a condenser. The top of condenser was attached to a gas trap containing a mixture of barium chloride solution (50 ml, 10%) and H₂O₂ (10 ml, 30%) to absorb SO₂ evolved during thermolysis by reflux or in 5 g of naphthalene at boiling tetraline (b.p. ca. 210°C) for 2 hr. The pyrolysate was evaporated *in vacuo*, and the resulting residue was extracted with chloroform, the extracts being washed several times with water. The combined washings were titrated with 0.1 *N* sodium carbonate solution to determine the amount of arene-sulfonic acid formed. The chloroform layer was evaporated to dryness and chromatographed over Kieselgel 60 with a (120 × 2.5 cm) glass column using the gradient elution technique as discussed. The barium sulfate precipitate

TABLE II Thermal Fragmentation Products of Phenacyl Aryl Sulfones **III** and **IV** in % Yield.

Decomposition Products %	III (Ph γ)	IV (p-tolyl)
CO	evolved	evolved
H ₂ S	1.8	2.6
Arene	10.1	8.8
Biaryl	7.0	6.5
Diaryl sulfide	10.8	12.6
Arenesulfonic acid	13.6	16.7
Acetophenone	11.0	9.4
Benzil	8.7	11.8
Diaryl sulfone	4.0	1.5
Arene thiol	12.1	15.5
Bibenzyl	7.5	—
Stilbene	8.6	—
Unresolved residue (g)	1.5	4.0

See footnotes Table I, and experimental section.

¹Heating of **III** in the presence of naphthalene as a radical trap where benzylnaphthalenes collected at b.p. 200–210°C/6 mm.Hg. analysed by glc into ratio of 70.3% 1- to 28.7% 2-isomer; 1-benzyl-naphthalene, m.p. and mm.p. 59–60°C; picrate (ethanol), m.p. 104–5°C; 2-benzyl-naphthalene, m.p. and mm.p. 55–56°C; picrate (ethanol), m.p. 95°C.

collected in the trap was filtered off, washed with water and dried to a constant weight. This was taken as a quantitative measure for the extruded SO₂ in the reaction (see Table II).

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