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MOLECULAR REARRANGEMENTS. VI. THERMOLYSIS OF α -(N-ARYL)BENZYL ARYL SULFIDES†

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In view of the significance of studying the effect of heat on organic compounds especially those containing nitrogen and/or sulfur, six substituted α -(N-aryl) benzyl aryl sulfides (4-9) were prepared and subjected to thermolysis at 200°C.

Surveying of the reaction products showed the formation of amines, benzylidene amines, sulfides, disulfides, dibenzyl, stilbene, benzthiazole, benzimidazole, tetraphenyl thiophene as principle products in variable ratios according to the type of the starting sulfide.

A mechanism involving the homolytic cleavage of the C—S and the C—N bond is suggested to rationalize the thermolysis products.

INTRODUCTION

Organic compounds containing sulfur and/or nitrogen have wide applications in industry and a vast number of these compounds have a pharmaceutical applications. Understanding of the thermal decomposition is also important as a part of the general investigation of this class of compounds and it has found a considerable attention in the literature.¹⁻²¹ Previous work in this laboratory showed that the thermal decomposition of sulfides and thioesters¹⁴⁻¹⁶ is characterized by a homolytic C—S bond fission. Further investigations were carried out on sulfides, sulfoxides and sulfones in the gas phase.¹

RESULTS AND DISCUSSION

Thermal decomposition of the title compounds, which serve as a model for the thermal decomposition of sulfur and nitrogen containing drugs, was probed through the experiments listed in Table 1. the selected compounds included α -(N-phenyl)benzyl phenyl sulfide (4), α -(N-phenyl)benzyl *p*-tolyl sulfide (5), α -(N-phenyl)benzyl benzyl sulfide (6), α -(N-phenyl)benzyl *p*-chlorophenyl sulfide (7), α -(N-benzyl)benzyl *p*-tolyl sulfide (8) and α -(N-*p*-tolyl)benzyl *p*-chlorophenyl sulfide (9).

Thermolysis of 4 at 200°C for 10 hours gave aniline, *N*-benzylideneaniline, diphenyl sulfide, diphenyl disulfide as principle products in addition to a small

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TABLE I
 Thermolysis of α -(*N*-aryl)benzyl aryl sulfides (4–9)

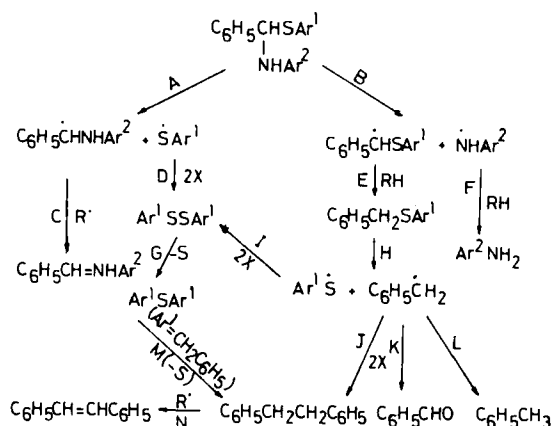
Entry	Compound	Decomposition products (%) ^a
1	(4) ^b	C ₆ H ₅ NH ₂ (27), C ₆ H ₅ CH=NC ₆ H ₅ (4), C ₆ H ₅ SC ₆ H ₅ (17), C ₆ H ₅ SSC ₆ H ₅ (48.5), C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅ (1), C ₆ H ₅ CH=CHC ₆ H ₅ (1.5).
2	(5)	C ₆ H ₅ NH ₂ (34), C ₆ H ₅ CH=NC ₆ H ₅ (8), <i>p</i> -CH ₃ C ₆ H ₄ SC ₆ H ₄ CH ₃ - <i>p</i> (27), <i>p</i> -CH ₃ C ₆ H ₄ SSC ₆ H ₄ CH ₃ - <i>p</i> (28), C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅ (1.0), C ₆ H ₅ CH=CHC ₆ H ₅ (2).
3	(6)	C ₆ H ₅ NH ₂ (26), C ₆ H ₅ CH=NC ₆ H ₅ (3.5), C ₆ H ₅ CH ₂ SCH ₂ C ₆ H ₅ (2), C ₆ H ₅ CH ₂ SSCH ₂ C ₆ H ₅ (1), 2-Phenylbenzthiazole (14), 1,2-Diphenylbenzimidazole (8), Tetraphenylthiophene (3.5), C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅ (20), C ₆ H ₅ CH=CHC ₆ H ₅ (22).
4	(7)	C ₆ H ₅ NH ₂ (26), C ₆ H ₅ CH=NC ₆ H ₅ (8), <i>p</i> -ClC ₆ H ₄ SC ₆ H ₄ Cl- <i>p</i> (25), <i>p</i> -ClC ₆ H ₄ SSC ₆ H ₄ Cl- <i>p</i> (38), C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅ (1.8), C ₆ H ₅ CH=CHC ₆ H ₅ (2).
5	(8)	C ₆ H ₅ CH ₂ NH ₂ (30), C ₆ H ₅ CH=NCH ₂ C ₆ H ₅ (4), <i>p</i> -CH ₃ C ₆ H ₄ SC ₆ H ₄ CH ₃ - <i>p</i> (20), <i>p</i> -CH ₃ C ₆ H ₄ SSC ₆ H ₄ CH ₃ - <i>p</i> (30), C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅ (14), C ₆ H ₅ CH=CHC ₆ H ₅ (2).
6	(9)	<i>p</i> -CH ₃ C ₆ H ₄ NH ₂ (22), C ₆ H ₅ CH=NC ₆ H ₄ CH ₃ - <i>p</i> (6), <i>p</i> -ClC ₆ H ₄ SC ₆ H ₄ Cl- <i>p</i> (22), <i>p</i> -ClC ₆ H ₄ SSC ₆ H ₄ Cl- <i>p</i> (23), C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅ (2), C ₆ H ₅ CH=CHC ₆ H ₅ (25).

^a Toluene and benzaldehyde were also detected in all runs by glc analysis.¹⁴

^b This experiment was performed in naphthalene and analysis of the product mixture gave, in addition to the products listed in entry 1, 2-naphthyl phenyl sulfide and 2-(*N*-phenyl) naphthyl amine.

amounts of dibenzyl and stilbene (Table 1, Entry 1). Similarly, 5 and 7 under the same conditions gave aniline, *N*-benzylideneaniline, dibenzyl, stilbene in addition to the corresponding sulfides and disulfides (Table 1, Entries 2 and 4). Benzyl amine and *p*-toluidene were identified among other products in the pyrolysates of 8 and 9, respectively (Table 1, Entries 5 and 6). On the other hand, thermolysis of 6 gave, on the contrary of the other sulfides (4, 5, 7, 8 and 9), dibenzyl sulfide and dibenzyl disulfide in only 2% and 1%, respectively, and dibenzyl and stilbene in large amounts (19% and 21%, respectively). Also, three heterocyclic products (2-phenylbenzthiazole; 1,2-diphenylbenzimidazole and 2,3,4,5-tetraphenylthiophene) were identified in the pyrolysate of 6.

It is clear from surveying of the reaction products in Table 1, that the investigated sulfides underwent C—S as well as C—N bond fission under the applied reaction condition. As reported by Dewar,²² synchronous multibond processes involving the making and/or breaking of two or more bonds, are likely to have activation energies that are roughly double those of analogous one-bond ones, explaining the predominance of the latter. Accordingly, the reaction products could be interpreted on the bases of non-synchronous homolytic fission of the C—S and the C—N bonds (Scheme 1, routes A and B, respectively) with the formation of the C₆H₅ĊNHAr² and ĤAr¹ radicals (route A) or the C₆H₅ĊHSAr¹ and ĤNHAr² radicals (route B). For example, amines (aniline, *p*-toluidine and benzyl amine) are formed from the corresponding Ar²NH radical through hydrogen abstraction (Scheme 1-F). Dibenzyl formed in case of 4, 5, 7, 8 and 9, although in low percentage, is of course from dimerization of benzyl

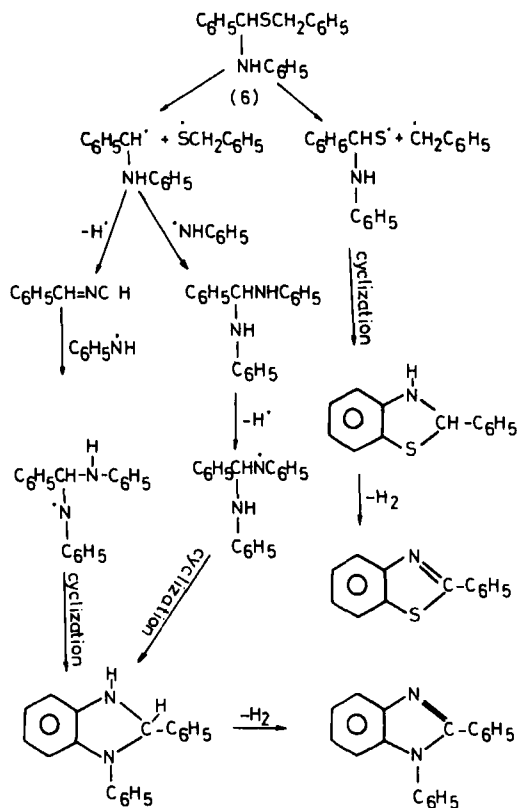


scheme 1 :

Comp.	Ar ¹	Ar ²	Comp.	Ar ¹	Ar ²
4	C ₆ H ₅	C ₆ H ₅	7	p-ClC ₆ H ₄	C ₆ H ₅
5	p-CH ₃ C ₆ H ₄	C ₆ H ₅	8	p-CH ₃ C ₆ H ₄	C ₆ H ₅ CH ₂
6	C ₆ H ₅ CH ₂	C ₆ H ₅	9	p-ClC ₆ H ₄	p-CH ₃ C ₆ H ₄

radicals (route J) produced by cleavage of benzyl aryl sulfide (route H) which is formed as intermediate from thioarylbenzyl radical $\text{C}_6\text{H}_5\dot{\text{C}}\text{HSAr}^1$ by hydrogen abstraction (Scheme 1-E). GC/MS analysis proved the presence of benzyl phenyl sulfide and benzyl *p*-tolyl sulfide in the pyrolysates of 4 and 5, respectively in only minute amounts. However, this is not unexpected because of the unstability of benzyl aryl sulfides under the reaction conditions,¹⁵ and partly because they are formed in small amounts as it is expected from the low percentage of the dibenzyl therefrom. Stilbene is formed from dibenzyl by hydrogen elimination¹⁶ (route N). The formation of *N*-benzylideneamines is not unexpected through dehydrogenation of the corresponding α -(*N*-aryl)benzyl radical ($\text{C}_6\text{H}_5\text{CHNHA}^2$) as discussed in route C.

Recombination of the arylthiyl radicals, formed through Scheme 1-A (mainly) and Scheme 1-H, affords diaryl disulfides¹ (routes D and I) from which diaryl sulfides are produced via sulfur extrusion²³ (route G). The presence of dibenzyl disulfide and dibenzyl sulfide (entry 3) in only small amounts, unlike the other sulfides and disulfides (entries 1, 2, 4, 5 and 6), is consistent with the higher reactivity of the (benzyl) C—S bond versus the (aryl) C—S bonds (route M). The formation of heterocyclic compounds upon thermolysis of 6 is undoubtedly due to readability of the (benzyl) C—S bond for cleavage under the applied conditions.¹⁴ To account for the formation of 1,2-diphenylbenzimidazole and 2-phenylbenzthiazole, we proposed the pathway depicted in Scheme 2. On the other hand, formation of 1,2,3,4-tetraphenylthiophene is possible, on the bases of our former confirmation, from in situ reaction of stilbene and sulfur already present as a degradation product in the reaction mixture.¹⁶



Scheme 2.

Naphthalene was used as a scavenger for anilino and phenylthiyl radicals by thermolysis of 4 in naphthalene for 15 hours under the same conditions. GC/MS analysis confirmed the presence of 2-naphthyl phenyl sulfide and 2--N-phenyl) naphthyl amine in the reaction mixture in addition to the other products identified in Entry 1 of Table 1.

In conclusion, the primary reaction of the investigated sulfides (4–9) under the thermolysis conditions is a non synchronous homolytic cleavage of the C—S and C—N bonds which leads to the formation of the intermediate radicals. These sulfur and nitrogen containing radicals undergo a series of reactions as shown in Scheme 1 to form the obtained reaction products.

EXPERIMENTAL

GC—MS analyses were carried out using Finnigan Mat 4032 Spectrophotometer with an Incos. data system using J & W Scientific Inc. 50 m DBI bonded phase capillary column (0.25 μ film thickness). Analytical tlc was carried out on a foil slides coated with polygram silica gel G/UV 254 nm (0.25 mm, Macherey, Nagel & Co.). All melting points were determined on kofler melting point, apparatus and were uncorrected.

The reaction products were identified using authentic samples, elemental analyses, mp, mmp, column chromatography, tlc, and GC/MS analyses.

Starting Materials (4–9). They were prepared via the addition of thiols to Schiff's bases as follows: Preparation of Schiff's bases (1–3): *N*-Benzyldeneaniline (1), *N*-benzyldenebenzylamine (2) and *N*-benzyldene *p*-toluidene (3) were prepared as reported.^{24–25} Schiff's base-thiol adducts (4–9): A solution of the Schiff's base (0.01 mole) and the thiol (0.1 mole) in 75 ml dry benzene was refluxed as described.²⁶ The products were recrystallized from ethanol. The adducts of 1 with each of thiophenol (4, m.p. 55°C, lit.²⁶ m.p. 55–56°C), *p*-toluenethiol (5, m.p. 72°C, lit.²⁶ m.p. 71–72°C), benzylthiol (6, m.p. 61°C, lit.²⁶ m.p. 61–62°C), *p*-chlorothiophenol (7, m.p. 72°C) as well as the adducts of 2 with *p*-toluenethiol (8, m.p. 32°C) and 3 with *p*-chlorobenzenethiol (9, m.p. 65°C), all gave satisfactory elemental (C, H, N and S) and spectroscopic analysis.

General procedure. In a 50 ml round flask equipped with an efficient reflux condenser there was placed 10 g of the Schiff's base-thiol adduct. The flask was heated for 10 hours at 200°C using temperature controlled heating mantle adjusted to the required temperature. The temperature was measured using a thermometer immersed in the reaction flask. The pyrolysate was extracted with ether (twice) and benzene (twice) and the whole extract was evaporated on water bath. The residue was treated on a silica gel column chromatogram to separate the charring materials which remained on the column. The eluents were collected, evaporated and the products were analysed by column chromatography, tlc, glc and gc/ms analysis. The experiments were performed twice and the results averaged (Table 1).

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