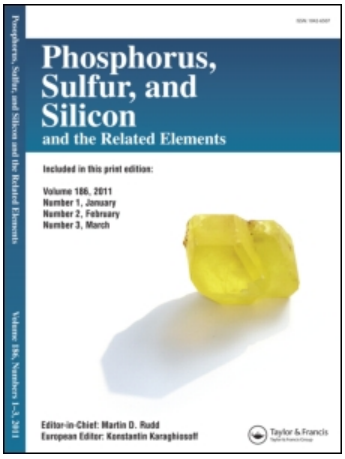

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The Thermal Fragmentation of Some *O*-Arylsulfonyl Diphenylhydroxylamine Derivatives

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The Thermal Fragmentation of Some *O*-Arylsulfonyl Diphenylhydroxylamine Derivatives

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Thermal fragmentation of O-Aryl-N,N-diphenylhydroxylamines ***I*** *and* ***II*** *were investigated. Neat heating in an atmospheric nitrogen afforded arenes, biaryl, diaryl sulfide, diphenylamine, diaryl sulfone, phenols, arenesulfonic acid, carbazole, and thianthrene. In the presence of isoquinoline as a radical trap,* ***I*** *gave 1-phenylisoquinoline as well as the previous products. Analogous results were obtained on heating of* ***I*** *in boiling tetraline, which lead to the formation of 1-hydroxytetraline, α-tetralone, and 1,1′-bitetralyl as the major products. A free-radical mechanism has been postulated to take place through the initial homolysis of N—O and S—O bonds to account for the identified products.*

Keywords Free radicals; hydroxylamines; thermolysis

INTRODUCTION

Arylhydroxylamines, especially their acyl or alkyl derivatives, have been implicated as carcinogens.[1–3] Furthermore, the chemistry of N-arylhydroxylamines has become of increasingly great importance in studies on the metabolism of nitrogen compounds.[4] The acid catalyzed rearrangement of N-phenyl hydroxylamines to p-aminophenol was first observed by Bamberger[5] and further extended by Ingold,[6] who revealed that the reaction involves an intramolecular nucleophilic rearrangement mechanism. It has been reported that the thermolysis and photolysis of N-phenyl hydroxylamines gave aniline, o- and p-aminophenols, azobenzene, and phenoxazine.[7,8] The biological activity of hydroxylamines prompted us to clarify the behavior of these compounds when subjected to a high temperature and reinvestigate such reactions in an effort to gain further information about a more generalized thermolytic mechanism.

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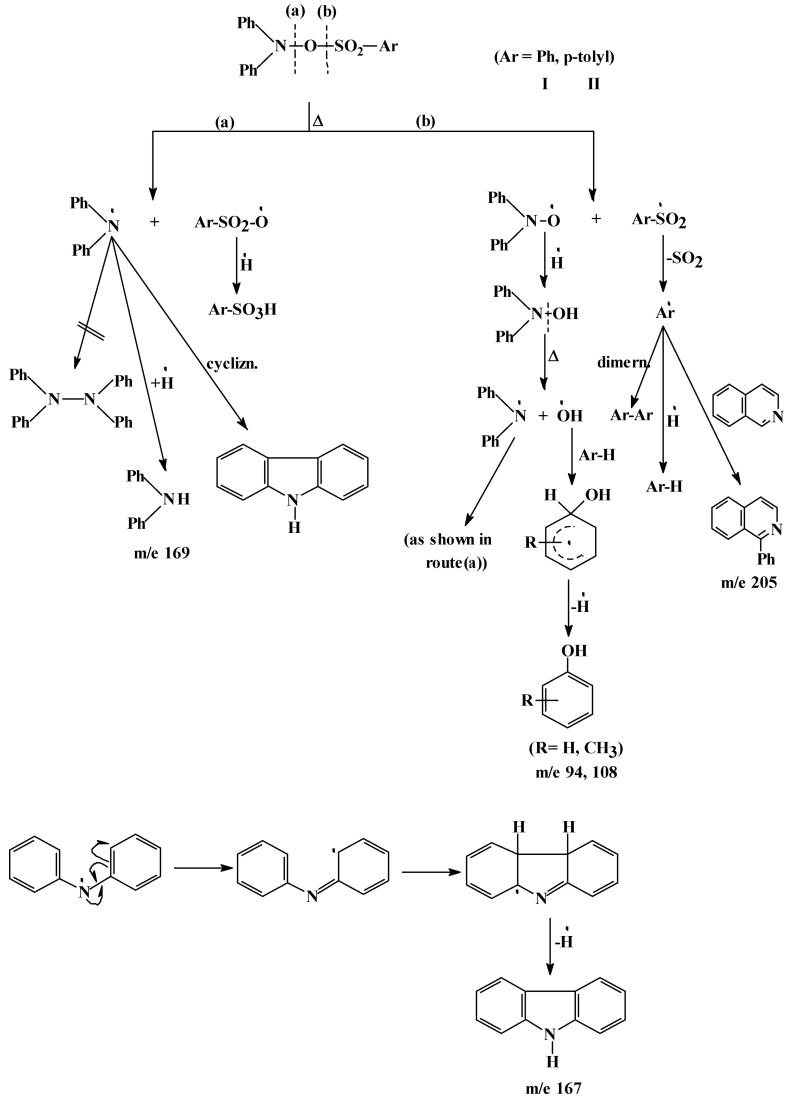
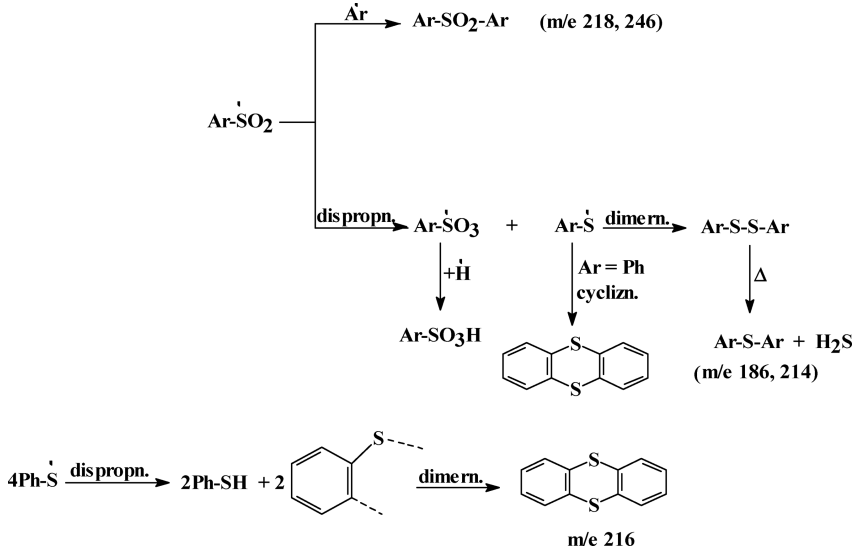
RESULTS AND DISCUSSION

The heating of O-phenylsulfonyl-N,N-diphenylhydroxylamine **I** leads to the formation of H_2S, SO_2, H_2O, benzene, biphenyl, benzenesulfonic acid, diphenyl sulfide, diphenyl-amine, diphenyl sulfone, phenol, carbazole, and thianthrene, as shown in Schemes 1 and 2. Although some products are present in small amounts due to the variable rate of decay



SCHEME 1

of the free radical intermediates, their presence is of great importance for mechanistic interpretation.



SCHEME 2

The formation of the identified products strongly points to a free radical mechanism starting the preferential homolysis of the N—O bond (Scheme 1, route (a)) rather than the S—O bond (route (b)) on the basis of bond energies.[9] As shown in Scheme 1, route (a) gave rise to N,N-diphenylaminyl and phenylsulfonyloxy radical pairs. The N,N-diphenylaminyl radicals may abstract hydrogen from a suitable source of the reaction medium to form diphenylamine (m/e 169).

A possible route for carbazole formation (m/e 167) could be suggested to take place through the intramolecular cyclization of diphenylaminyl radical.[10] In contrast, the phenyl-sulfonyoxyl radical may abstract hydrogen from the reaction medium to give benzenesulfonic acid.[11]

It may be noted that tetraphenylhydrazine was not formed as the thermal product of the dimerization of the diphenylaminyl radical. Such a result may be attributed to the instability of the N—N bond.[12]

Another competing pathway for the thermolysis of O-phenylsulfonyl-N,N-diphenyl-hydroxylamine **I** is the homolysis of the S—O bond (Scheme 1, route (b)) furnishing N,N-diphenylaminyloxy and phenylsulfonyl radical pairs. The diphenylaminyloxy radical may abstract hydrogen from a suitable source to give N,N-diphenylhydroxylamine, which

subsequently tends to decompose thermally under the same conditions into the N,N-diphenylaminyl radical and water.

The formation of carbazole by the two routes (a), (b) in Scheme 1 may account for its high yield among the isolated products.

The formation of phenol (m/e 94) can be assumed to proceed through a coupling of a hydroxylradical with a phenyl radical, which is readily available in the reaction medium,[13] (Scheme 1).

The desulfurization of a phenylsulfonyl radical could account for the liberation of sulfur dioxide and the formation of benzene and biphenyl through the H-abstraction and dimerization of phenyl radical, respectively.[14]

On the other hand, Scheme 2 includes that the benzenesulfonyl radical may couple with the phenyl radical to afford diphenyl sulfone (m/e 218) or it is disproportionate into phenylthiyl and benzenesulfonyloxy radical pairs.[15] The phenylthiyl radical may dimerize into diphenyldisulfide, which ultimately decomposes into hydrogen sulfide and diphenyl sulfide (m/e 186),[16] as shown in Scheme 2. The benzenesulfonyloxy radical may abstract hydrogen to yield benzenesulfonic acid.

The formation of thianthrene (m/e 216) can be explained on the basis of a disproportionation of the phenylthiyl radical,[17] as depicted in Scheme 2.

Also, the thermal fragmentation of O-toluenesulfonyl-N,N-diphenylhydroxylamine **II** under the same conditions gave H_2S, SO_2, H_2O, toluene, p,p-ditolyl, diphenylamine, p,p-ditolyl sulfone, p-cresol, p,p-ditolyl sulfide, toluene sulfonic acid, and carbazole (Schemes 1 and 2). The formation of these observed products was assumed to take place via the same mechanism suggested previously in Schemes 1 and 2. The results are given in Table I.

Moreover, the thermal fragmentation of O-benzenesulfonyl-N,N-diphenylhydroxylamine **I** in the presence of isoquinoline as a radical trap under the conditions used yielded the same products as mentioned before in addition to 1-phenylisoquinoline (m/e 205), as shown in Scheme 1. The trapping of phenyl radicals by isoquinoline may be considered as further evidence for free radical reactions.

The thermal fragmentation of **I** under reflux in boiling tetraline (210°C) formed 1-hydroxytetraline, α-tetralone and 1,1′-bitetralyl as the major products beside the same products as mentioned before, as shown in Schemes 1, 2 and 3.

A possible pathway for the formation 1-hydroxytetraline (m/e 148), α-tetralone (m/e 146), and 1,1′-bitetralyl (m/e 262) through a process of initial hydrogen abstraction[11] from the solvent nuclei (tetraline) to form a 1-tetralyl radical that interacts with hydroxyl radical, which

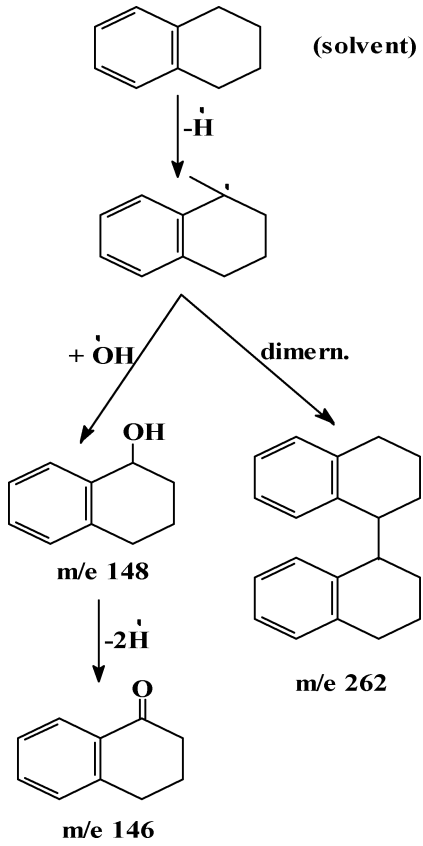
TABLE I Thermolysis Products of Arylsulfonylhydroxylamines I and II in Yield %

Products[a]	I (Ar = Ph)	II (Ar = p-Tolyl)	I[b]	I[c]
SO_2[d]	4.1	3.8	2.8	2.6
Biaryl	9[e]	7[f]	8[e]	6[e]
Phenols	7[g]	4[h]	6[g]	—
Diphenylamine	10.6	8.2	7.1	6.5
Diaryl sulfide	6[i]	7[j]	6[i]	5[i]
Diaryl sulfone	7[k]	9[l]	6[k]	6[k]
Arenesulfonic acid	13.5[m]	14[n]	10[m]	9[m]
Thianthrene	14	13	11	8
Carbazole	11	15	13	8
α-Tetralone[o]	—	—	—	12
1-Hydroxytetraline[p]	—	—	—	14
1,1′-Bitetralyl[q]	—	—	—	16
1-Phenylisoquinoline	—	—	8.2	—
Unresolved residue (g)	(0.2)	(0.35)	(0.41)	(0.12)

[a] H_2S was detected by chemical means; H_2O as a trace amount.
[b] The heating of **I** in the presence isoquinoline as a radical trap.
[c] Heating of **I** in anhydrous boiling tetraline as aromatic solvent.
[d] Estimated as $BaSO_4$.
[e] Biphenyl.
[f] p,p-Ditolyl.
[g] Phenol.
[h] p-Cresol.
[i] Diphenyl sulfide.
[j] p,p-Ditolyl sulfide.
[k] Diphenyl sulfone.
[l] p,p-Ditolyl sulfone.
[m] Benzenesulfonic acid.
[n] Toluenesulfonic acid.
[o] Collected at b.p. 113–116°C/6 Torr; n_D^{20}: 1.5679; m/e 146.
[p] Collected at b.p. 102–115°C/2 Torr as pale yellow oil; n_D^{20}: 1.5638; phenyl. urethane derivative (ligroin), m.p. and m.m.p. 120–122°C; m/e 148.
[q] Eluted from column chromatography using a 2% mixture of ether-pentane, m.p. and m.m.p. 113°C; on heating with elemental sulfur give bis-naphthylene;[26] m/e 262.

is readily available in the reaction medium followed by oxidative dehydrogenation or the 1-tetralyl radical, may undergo dimerization,[13,18] respectively.

It is noticed that phenol was absent from the pyrolysate as demonstrated by GC/MS. This is because the hydroxyl radical prefers to couple with the 1-tetralyl radical to form 1-hydroxytetraline, hence the consumption of a hydroxyl radical due to the presence of another competing pathway, such as the H-abstraction (Scheme 3).



SCHEME 3

EXPERIMENTAL

All melting points are uncorrected. The IR spectroscopic analyses were carried out on a Pye-Unicam spectrophotometer model SP-3-100 using the KBr wafer technique. ^{1}H NMR spectra were recorded on a Varian EM-390 90 MHz spectrometer in suitable deuterated solvents using TMS as an internal standard. TLC was carried out on glass plates (10 × 3 cm) coated with silica gel (25–40 mesh) eluted with ether-pentane (1:4 v/v). GC/MS analyses were carried out using a Finnigan MAT SSQ 7,000 spectrophotometer with 5% (phenylmethylpolysiloxane) using a 30 m DB-1 capillary column. Products were identified either by co-injection with authentic samples and/or by comparison with known GC/MS library fragmentation pattern. GLC was carried out using a Perkin-Elmer model Sigma 3B apparatus using a column

4 ft × 4 mm packed with SE 30 over Chromosorb W (35–80 mesh) or 10% SE on Celite (60–80 mesh) at 200°C, using nitrogen as a carrier gas. Microanalyses were performed using a Perkin-Elmer 240 C microanalyzer. Separation on column chromatography packed with kieselgel 60 (0.040–0.063 mm) using successive solvents: pet. ether (40–60°C), pet. ether (60–80°C), benzene, and ether-pentane as mixtures.

Starting Materials

O-benzenesulfonyl-N,N-diphenylhydroxylamine **I**, crystallized from ethanol, m.p. 142–145°C, (lit.[19], m.p. 145°C).

O-toluenesulfonyl-N,N-diphenylhydroxylamine **II**, crystallized from ethanol, m.p. 122–124°C (lit.,[19] m.p. 122–125°C).

The General Method for the Thermal Fragmentation of Hydroxylamines I and II

Hydroxylamines **I** and **II** (1 g) were placed in 50-mL round flask fitted with an efficient reflux condenser and gas inlet and were heated using a temperature-controlled heating mantle adjusted to the desired temperature (ca. 200°C) for 2 h either alone or in isoquinoline (0.5 mL) as radical scavenger, while **I** was heated in anhydrous tetraline (distilled over lithium aluminum hydride under nitrogen) as a solvent. The temperature was measured using a thermometer immersed in the reaction flask. The top of the condenser was attached to a gas trap containing a mixture of barium chloride (10 mL, 10%) and hydrogen peroxide (2 mL, 30%) to absorb SO_2 evolving during thermolysis and driven off by a stream of dry nitrogen, which passed through the gas inlet into the reaction vessel. The gas evolved was detected by standard chemical means (H_2S was detected by lead acetate). After decomposition was complete as judged by TLC monitoring, the pyrolysate was distilled using a microdistillation system at reduced pressure for the separation of low boiling-points products such as benzene, toluene, phenol, p-cresol, diphenylamine, and diphenyl sulfide. Benzene was identified by GLC analysis; it showed a single peak at 0.7 min at 90°C with an authentic sample. Toluene was collected at b.p. 60–65°C/3 Torr, and GLC analysis revealed a single peak at 1.0 min at 90°C, comparable with an authentic sample. Diphenylamine was collected at b.p. 120–125°C/3 Torr; m.p. and m.m.p. 53°C; N-benzoyl derivative, m.p. and m.m.p. 179–180°C; m/e 169. Diphenyl sulfide[20] was collected at 110–115°C/3 Torr and was identified as diphenyl sulfone by oxidation using H_2O_2/acetic acid, m.p. and m.m.p. 127°C; m/e 186. Phenol was collected at 70–75°C/5 Torr; picrate derivatives, m.p. and m.m.p. 83°C; m/e 94; it was further identified

by a chemical test.[21] p-Cresol was collected at b.p. 60–65°C/ 6 Torr; benzoyl derivative, m.p. and m.m.p. 71–72°C; m/e 108. The remaining (nondistillable) residue was dissolved in ether and shaken several times with ethanolic potassium hydroxide solution (Claisen's solution) to dissolve the resulting phenols. The Claisen extract was acidified with 2N HCl, and the liberated phenols were extracted with ether. Phenols (in part) were separated and identified either by vacuum distillation or by chemical tests as mentioned before. The neutral fraction was extracted with ether. Ether was evaporated in vacuo. The remaining, in part, was extracted with chloroform and washed several times with water. The combined washings were titrated with 0.1 N sodium carbonate solution to determine the amount of arenesulfonic acid formed. Also, the barium sulfate collected in the trap was filtered off, washed with water, dried to a constant weight, and taken as a quantitative measure for the extruded sulfur dioxide in the reaction. The another part of the remaining residue was separated by column chromatography on Kieselgel 60 (0.040–0.063 mm) using an gradient elution technique as follows: Biphenyl was eluted from column chromatography using a mixture of pet. ether (40–60°C), pet. ether (60–80°C) (1:2 v/v), m.p. and m.m.p. 71–72°C; 4,4′-dinitroderivative, and m.p. 234°C, and it showed a GLC peak at 3.3 min at 140°C. p,p-Ditolyl[22] was eluted from column chromatography using pet. ether (60–80°C), m.p. and m.m.p. 125°C; ^{1}H NMR, δ7.2 (m, 4H), 7.4–7.5 (m, 4H), 2.3–2.4 (s, 6H); m/e 182. Diphenyl sulfone was eluted from column chromatography using a mixture of pet.ether (60–80°C)-benzene (1:1 v/v), m.p. and m.m.p.127°C; m/e 218. p,p-Ditolyl sulfide[23] was eluted from column chromatography using a mixture pet. ether (60–80°C)-benzene (2:1 v/v), m.p. and m.m.p. 55–58°C; its sulfone m.p. and m.m.p. 159°C; m/e 214. Thianthrene[20] was eluted from column chromatography using benzene, m.p. and m.m.p. 158–160°C; ^{1}H NMR δ 7.2 (m, 4H), 7.4–7.5 (m, 4H); m/e 216. Carbazole[24] was eluted from column chromatography using a mixture 1% ether-pentane, m.p. and m.m.p. 242–245°C; picrate m.p. 185°C. Calcd. for $C_{12}H_9N$: C, 86.23; H, 5.39; N, 8.38%. Found: C, 85.75; H, 5.47; N, 8.78%; m/e 167. 1-Phenylisoquinoline[25] was eluted from column chromatography using pet. ether (60–80°C)-benzene (3:2 v/v), m.p. and m.m.p. 95°C; picrate (ethanol), m.p. 164°C; m/e 205. The products are summarized in Table I.

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