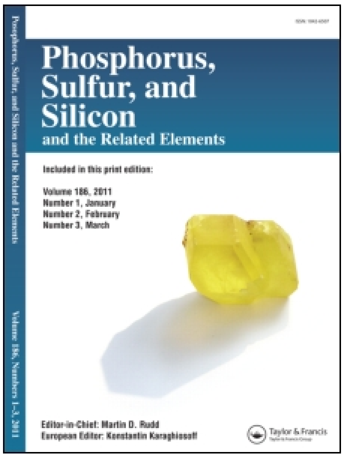

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MOLECULAR REARRANGEMENT OF SULFUR COMPOUNDS(VII).† PYROLYSIS OF ARENESULFONYLHYDRAZINE DERIVATIVES

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N-Phenyl-N'-arenesulfonylhydrazine(I–II) on pyrolysis by refluxing in an atmosphere of nitrogen at ca. 240°C give SO_2, H_2S, NH_3, arene, biaryl, aniline, azobenzene, diaryl sulfide, diaryl sulfone, arenesulfonic acid, phenyl hydrazine and carbazole derivatives. N-Benzylidene-N'-benzenesulfonylhydrazone(III) on similar treatment gives the previous products in addition to benzonitrile, bibenzyl, stilbene, 2-phenylindole and 2,3,4,5-tetraphenylthiophene. The observed results have been interpreted in terms of a free radical mechanism involving the homolysis of N—N and S—N bonds.

Key words: Molecular rearrangement, pyrolysis, sulfonyl hydrazines.

INTRODUCTION

In continuation of our studies on photolytic and pyrolytic fragmentation mechanisms of model organic compounds, it was reported[1] that *p*-tolylsulfonylhydrazones, on irradiation gave azines and sulfones.

Recently[2] it was reported that pyrolysis of 1-aroyl-2-phenylsulfonyl hydrazine yielded diphenyldisulfide and the corresponding acid and aldehyde by an obscure mechanism. This finding prompted us to reinvestigate this a reaction in order to clarify its mechanism of fragmentation.

RESULTS AND DISCUSSION

The formation of the identified products strongly points to a free radical mechanism starting the preferential homolysis of the N—N bond (Scheme 1, route a) rather than the N—S bond (route b) on the basis of bond energies being of the order of 44 and 116 K cal/mol^{-1} resp.[3] As shown in Scheme 1, route (a) gave arenesulfonamidyl and anilino radical pairs. The former may abstract hydrogen from the reaction medium forming arenesulfonamide. This compound subsequently tends to decompose thermally under the same conditions into arene sulfonyl radicals and ammonia.[4,5] Desulfurization of arenesulfonyl radicals could account for liberation of sulfur dioxide and formation of an aryl radical which may form the corresponding diaryl

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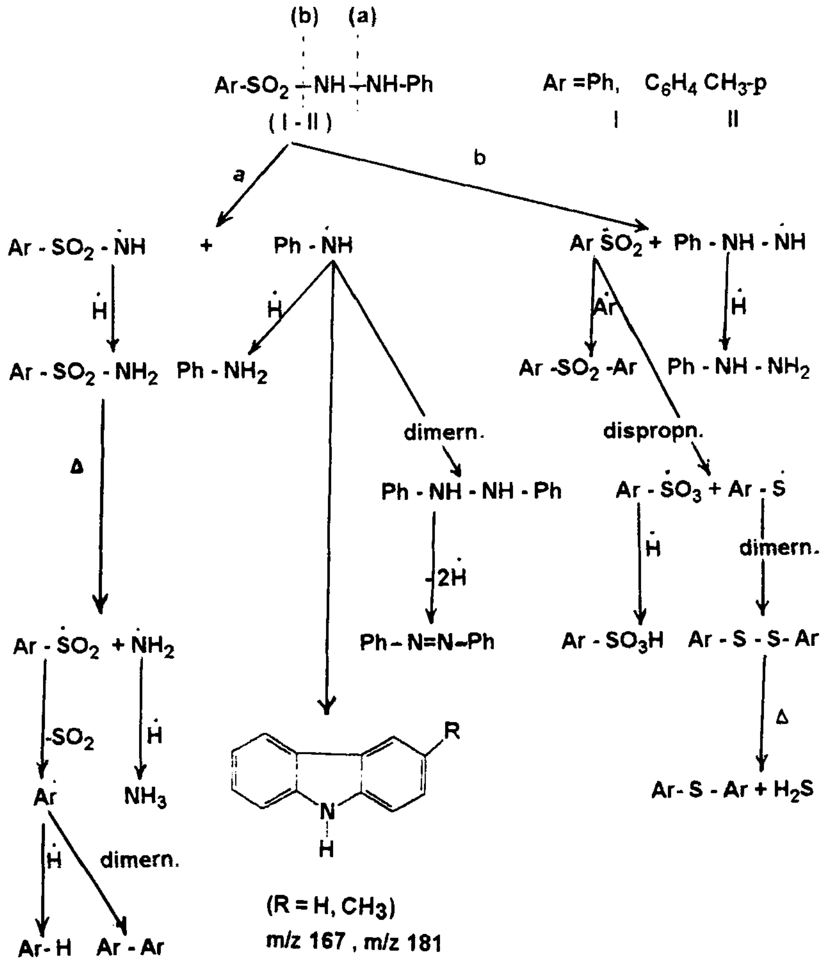


(Scheme 1)

by dimerization and arene by H-abstraction. Whereas, the anilino radical may abstract hydrogen to afford aniline. N—N dimerization of anilino radical leads to the formation of hydrazobenzene that ultimately dehydrogenates into azobenzene.[6]

A possible route for carbazole and 3-methylcarbazole formation could be suggested to take place through coupling anilino and aryl free radicals followed by cyclization to *o*-aminobiphenyl[7] as shown in (Scheme 1, route a).

Furthermore, the formation of phenylhydrazine, diaryl sulfide, arenesulfonic acid and diaryl sulfone may be explained as taking place through homolysis of the N—S bond (route b) yielding arenesulfonyl and phenylhydrazyl radical pairs. The latter may abstract hydrogen from the reaction medium to give thermally stable phenylhydrazine under the same conditions as shown experimentally, while the former may couple with the aryl radical to afford the diaryl sulfone or it may disproportionate into arylthiyl and arenesulfonic free radicals[8] which subsequently may abstract hydrogen forming arene sulfonic acid. Whereas the arylthiyl radicals may dimerize into diaryldisulfide which ultimately decomposes into hydrogen sulfide and diaryl sulfide[9] is shown in Scheme 1.

Similar results have also been obtained by pyrolysis of N-benzylidene-N′-benzenesulfonyl hydrazone(III) under the same conditions to give rise to the previously mentioned products namely; NH_3, SO_2 benzene, biphenyl, diphenyl sulfide, benzenesulfonic acid and diphenyl sulfone which could be interpreted as mentioned before in the decomposition of N-phenyl-N′-arenesulfonylhydrazine(I, II).

The formation of benzonitrile and 2-phenylindole can be assumed to proceed through the homolysis of the N—S bond (Scheme 2, route a) form benzene sulfonamidyl and benzaliminyl radical pairs. The fate usually occurring with the first mentioned radicals was already discussed (Scheme 1), whereas the latter lose hydrogen to form benzonitrile or may isomerize followed by coupling with benzyl radical to afford phenyl benzylimine (C—C rather than C—N coupling) which undergoes cyclization into 2-phenylindole.[10]

On the other hand, Scheme 2, route (b) also includes N—N bond homolysis to give benzenesulfonyl and benzenehydrazonyl radical pairs. The former was discussed and mentioned previously (see Scheme 1), however the latter ones may isomerize and followed by extrusion of nitrogen[11] to generate benzyl free radicals. They are considered as precursor of bibenzyl and stilbene obtained by dimerization and subsequent, dehydrogenation resp.

A possible pathway for the formation of tetraphenylthiophene could be the interaction of stilbene with sulfur radicals. These species are available in the reaction medium as reported earlier[12] (Scheme 2).

EXPERIMENTAL

Melting points were determined on a Kofler melting point apparatus and are uncorrected. Column chromatographic separations were carried out using a 100 × 2.5 cm glass column packed with kieselgel 60 (0.040–0.063 mm) using successively pet.-ether (40–60°C), pet.-ether (40–60°C),-pet.-ether (60–80°C) mixtures, pet. ether (60–80°C)-benzene mixtures, benzene-ether mixtures, ether, ether-methanol mixtures, and finally methanol. Thin-layer chromatography was performed using 10 × 3 cm glass plates coated with silica gel and eluted with ether-pentane (1:4 v/v). GLC analyses were carried out on a Perkin-Elmer Sigma 3B instrument, using a 4 ft × 4 mm column packed with 30% SE 30 on Chromosorb W (35-80 mesh) at 180°C, using nitrogen as a carrier gas. GC-MS analyses were carried out using an El-SSQ7000 apparatus.

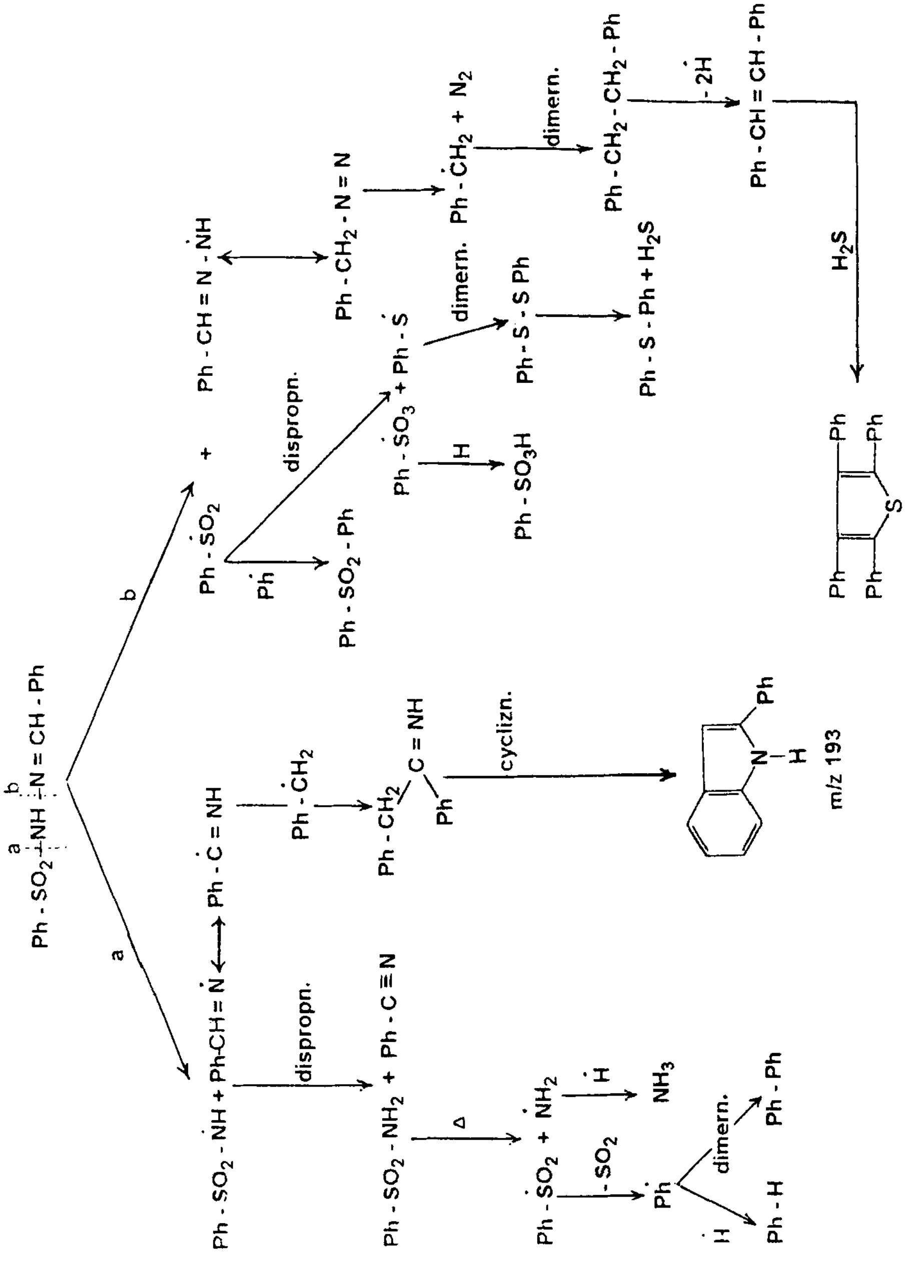
Starting Materials

N-Phenyl-N′-benzenesulfonylhydrazine(I), crystallized from ethanol, lit.,[13] m.p. 146–48°C.
N-Phenyl-N′-*p*-tolylsulfonylhydrazine(II), crystallized from ethanol, lit.,[14] m.p. 155–7°C.
N-Benzylidene-N′-benzenesulfonylhydrazone(III), crystallized from ethanol, lit.,[15] m.p. 110–12°C.

It is worth mentioning that a number of preliminary experiments were carried out to determine the proper temperature for pyrolysis. The decomposition of I and II starts above 220°C and that for III at 230°C. Also it was found that 240°C is the lowest temperature at which the conversion of the sulfonylhydrazines(I–III) was complete at the end of pyrolysis.

General Procedure

The sulfonylhydrazine (10 g) was placed in a 50 ml round flask fitted with an efficient reflux condenser, gas inlet and heated, using a temperature controlled heating mantle adjusted to the desired temperature, for 2 hours. 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 (50 ml, 10%) and hydrogen peroxide (10 ml, 30%) to absorb SO_2 evolving during pyrolysis and driven off by a slow


Ph - SO2 - NH - N = CH - Ph
a
b
Ph - SO2 - NH + Ph-CH = N ⟷ Ph - C = NH
Ph - SO2 + Ph - CH = N - NH
dispropn.
Ph - SO2 - NH2 + Ph - C ≡ N
Δ
Ph - SO2 + NH2
H
NH3
-SO2
Ph
H
Ph - H
dimern.
Ph - Ph
Ph - CH2
Ph - CH2
C = NH
Ph
cyclizn.
N - H
Ph
m/z 193
Ph
Ph - SO2 - Ph
dispropn.
Ph - SO3 + Ph - S
H
Ph - SO3H
dimern.
Ph - S - S Ph
Ph - S - Ph + H2S
Ph - CH2 - N = N
Ph - CH2 + N2
dimern.
Ph - CH2 - CH2 - Ph
- 2H
Ph - CH = CH - Ph
H2S
Ph
Ph
S
Ph
Ph

(Scheme 2)

TABLE I

Products of pyrolysis of arene sulfohydrazines(I–III) in gram (%)

STARTING HYDRAZINE DERIVATIVES	I	II	III
Ammonia	evolved	evolved	evolved
Hydrogen sulfide	evolved	evolved	evolved
Sulfur dioxide[a]	0.18 (1.8)	0.14 (1.4)	0.1 (1)
Arene	trace[b]	trace[c]	trace[b]
Biaryl	0.9[d] (9)	1.0[e] (10)	0.25[d] (2.5)
Diaryl sulfide	0.8[f] (8)	1.2[g] (12)	0.82[f] (8.2)
Diaryl sulfone	1.3[h] (13)	1.4[i] (14)	1.1[h] (11)
Bibenzyl [j]	---	---	1.0 (10)
trans - Stilbene[k]	---	---	0.7 (7)
Benzonitrile[l]	----	----	1.2 (12)
Aniline[m]	1.5 (15)	1.3 (13)	--
Azobenzene[n]	0.8 (8)	0.6 (6)	---
Arenesulfonic acid	1.5[o] (15)	1.6[p] (16)	1.3[o] (13)
Phenylhydrazine[q]	0.8 (8)	0.6 (6)	---
2 - Phenylindole[r]	---	---	1.7 (17)
Carbazole derivatives	1.8[s] (18)	1.7[t] (17)	---
2,3,4,5 - Tetraphenyl-thiophene[u]	----	---	1.4 (14)
Residue	0.4	0.3	0.33

a) Estimated as $BaSO_4$;b) Benzene was identified by glc analysis. It showed a single peak at o.7 min at 90°C identified with an authentic sample;c) Toluene; 2,4 dinitro derivative m.p. and mixture m.p. 71 °C and identified by glc analysis; revealed a peak at 1 min. at 90 °C, comparable with an authentic sample.

d) Biphenyl , m.p. and mixture m.p. 71-2°C; 4,4'- dinitro derivative, m.p. 234°C .

e) p,p-Ditolyl;m.p. and mixture m.p. 125 °C; f) Diphenyl sulfide, identified as diphenyl sulfone by oxidation using with H_2O_2/acetic acid m.p. and mixture m.p. 127°C;g) p-Ditolyl sulfide, m.p and mixture m.p. 57-8°C; h) Diphenyl sulfone, m.p. and mixture m.p. 127°C;i) p - Ditolyl sulfone, m.p. and mixture

m.p. 159°C;j) M.p. 52°C; 4,4'-dinitro dervative, m.p. and mixture m.p. 180°C;k) M.p. and mixture m.p. 125°C;l) B.p. 150-5°C/13 mm.Hg.; on hydrolysis gives benzoic acid , m.p. and mixture m.p. 120°C;m) B.p. 80-5°C/13mm.Hg.; acetyl derivative m.p. and mixture m.p. 113-4°C;

n) M.p. and mixture m.p. 60°C;o) Benzenesulfonic acid;p) p-Toluenesulfonic acid.

q) B.p. 185-90°C/13mm. Hg; its hydrochloride, m.p. and mixture m.p. 250-2°C;r) M.p . 188-89°C; picrate derivative m.p. and mm.p. 127°C. Calcd.for $C_{14}H_{11}N$:C,87.05;H,5.70;N,7.25%. Found:C,86.82;H,5.24;N,7.94%;MS(m/e) 193.s) M.p. and mixture m.p. 245°C; picrate derivative m.p. and mixture m.p. 185-6°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% ; MS(m/e)167;t) M.p. and mixture m.p. 207°C; picrate derivative m.p. and mm.p. 179-80°C; Calcd. for $C_{13}H_{11}N$:C,86.19;H,6.08;N,7.73%. Found:C,86.62;H,5.76;N,7.62;MS(m/e) 181;u)M.p. and mixture m.p. 184-5°C;Calcd. S:8.71;Found S:8.26%.

stream of dry nitrogen which was passed through the gas inlet into the reaction vessel. After decomposition was complete, the pyrolysate was distilled at atmospheric pressure up to 180°C in order to separate low boiling products, such as benzene, toluene, and aniline.

The nondistillable residue 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. The dried chloroform layer was evaporated to dryness and chromatographed over silica gel column using the gradient elution technique.[16]

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.

Preparation of Reference Samples

Diphenyl sulfide,[17] oil, b.p. 115°C/3 mm, Hg.
Diphenyl sulfone,[18] crystallized from ethanol, m.p. 127°C.
p,p-Ditolyl,[19] crystallized from pet. ether (60–80°C), m.p. 125°C.
p-Ditolyl sulfide,[20] crystallized from ethanol, m.p. 57–8°C.
p-Ditolyl sulfone,[21] crystallized from water, m.p. 159°C.
3-Methylcarbazole,[22] crystallized from ethanol, m.p. 209°C.
Bibenzyl,[23] crystallized from ethanol, m.p. 50–2°C.
trans-Stilbene,[24] crystallized from ethanol, m.p. 124°C.
2,3,4,5-Tetraphenylthiophene,[25] crystallized from benzene-pet. ether (60–80°C (1:1 v/v), m.p. 185°C.

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