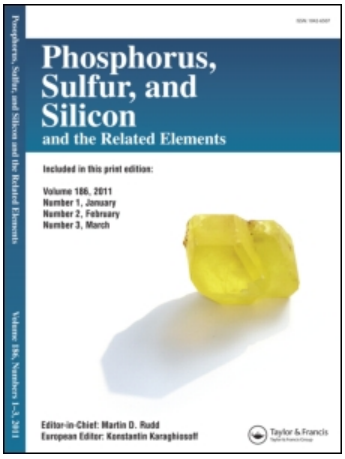

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MOLECULAR REARRANGEMENTS OF SULFUR COMPOUNDS THERMOLYSIS AND PHOTOLYSIS OF KETOXIME ARENESULFONATES

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Thermolysis of acetophene oxime arenesulfonate in boiling tetralin for 2 hrs affords NH_3, SO_2, H_2O, arene, acetophenone, benzonitrile, 2-methylbenzoxazole, acetanilide, arenesulfonic acid, biaryl, diarylsulfide, diarylsulfone, diaryldisulfone, arylammonium sulfonate, ammonium sulfite, phenol and p-cresol. Similar results were obtained on thermolysis of benzophenone oxime arenesulfonates besides benzanilide, benzonitrile, benzophenone, 2-phenylbenzoxazole. Photolysis of these ketoxime arenesulfonates afford acetanilide, benzanilide, acetophenone, phenol, p-cresol, biaryl, diarylsulfones and arenesulfonic acid. A free radical mechanism was suggested to account for the observed results.

Key words: Molecular rearrangement; thermolysis and photolysis; ketoxime arenesulfonates.

INTRODUCTION

Benzophenone oxime benzenesulfonate changes slowly on standing and more rapidly on exposure to U.V. light and instantaneously on melting to unstable oil readily hydrolyzed to benzanilide and benzenesulfonic acid.[1] Acetophenone oxime benzenesulfonate also decomposes exothermally in benzene and the products contain N,N-diphenylacetamidine and acetanilide. Other ketoxime arylsulfonates undergo spontaneous Beckmann rearrangement,[2] but the oily products were only characterized by hydrolysis. Amidine is produced in good yield when ketoxime sulfonates undergo the Beckmann rearrangement in the presence of ammonia or amines.[3] This prompted us to investigate the mechanistic behaviour of thermolysis and photolysis of ketoximearenesulfonates.

RESULTS AND DISCUSSION

Acetophenone oxime benzenesulfonate (**1**), and/or acetophenone oxime p-toluenesulfonate (**2**) in boiling tetralin gives rise to ammonia, sulfur dioxide, water, acetophenone, acetonitrile, 2-methylbenzoxazole, acetanilide in addition to the formation of the corresponding arene, biaryl, diarylsulfone, arylammonium sulfonate, ammonium sulfite and arenesulfonic acid.

Isomerization of these oxime esters yields imidosulfonates[2] through the 1,2 shift of phenyl migration followed by rearrangement. The instability of the imidosulfonate led Chapmann[4] to report that the final products obtained from benzophenone oxime sulfonate and the corresponding acetophenone oxime sulfonate are N-benzoyl and N-acetyl benzenesulfonanilide. The absence of these products may be

attributed to the hydrolysis of the imidosulfonates to anilides and arenesulfonic acid.

The formation of the separated products involves homolysis of the (N—O) bond (route a) which requires a lower energy to sever than the (S—O) bond (route b) according to the bond energy values.[5]

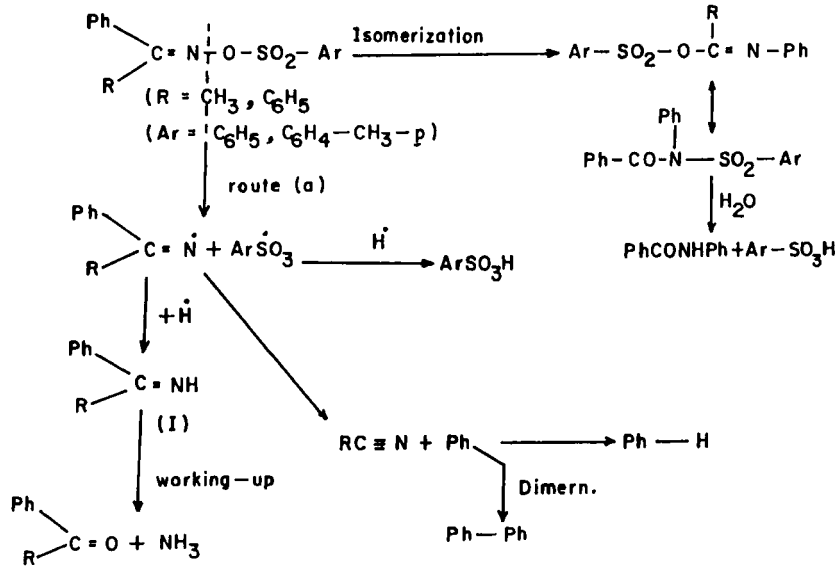
Homolysis of (N—O) bond gives iminyl[6] and arenesulfonyloxy[7] radicals which subsequently may abstract hydrogen from the solvent forming imine (**I**), which is considered to be the precursor of ammonia, and the corresponding ketone during working-up. The corresponding arenesulfonyloxy radicals abstract hydrogen forming phenols as shown in Scheme (1).

Another competing pathway implies homolysis of the (S—O) bond[8] by route (b) to give arenesulfonyl and iminoxyl radical pairs as shown in Scheme (2).

Dimerization of the arenesulfonyl free radical through (S—S) coupling leads to the formation of the corresponding diaryl disulfone. The low yield of diarylsulfones gives a clue to their instability, especially in the case of p.ditolyl disulfone.[9] On similar grounds, sulphinylsulfonates that may be formed from dimerization through (S—O) coupling are unlikely to be formed or even if they are formed they will rapidly dissociate into sulfinyl and sulfonate radical pairs. The whole process appears as disproportionation. The coupling of a sulfonyl radical with a sulfonate radical could give sulfonic anhydride which easily undergoes hydrolysis during work-up procedure to give the corresponding sulfonic acid.

Desulfonylation of some arenesulfonyl radicals could account for the liberation of sulfur dioxide.[10,11] The formation of aryl radicals may then participate in other successive reactions forming the corresponding diaryl[12] by dimerization, arene by H abstraction, or diarylsulfide by coupling with the aryl thiyle radical (**II**).

The iminoxyl radical (**III**) may undergo the Beckmann rearrangement[13,14] into the corresponding N-acylanilide. The formation of acetanilide in the case of ace-



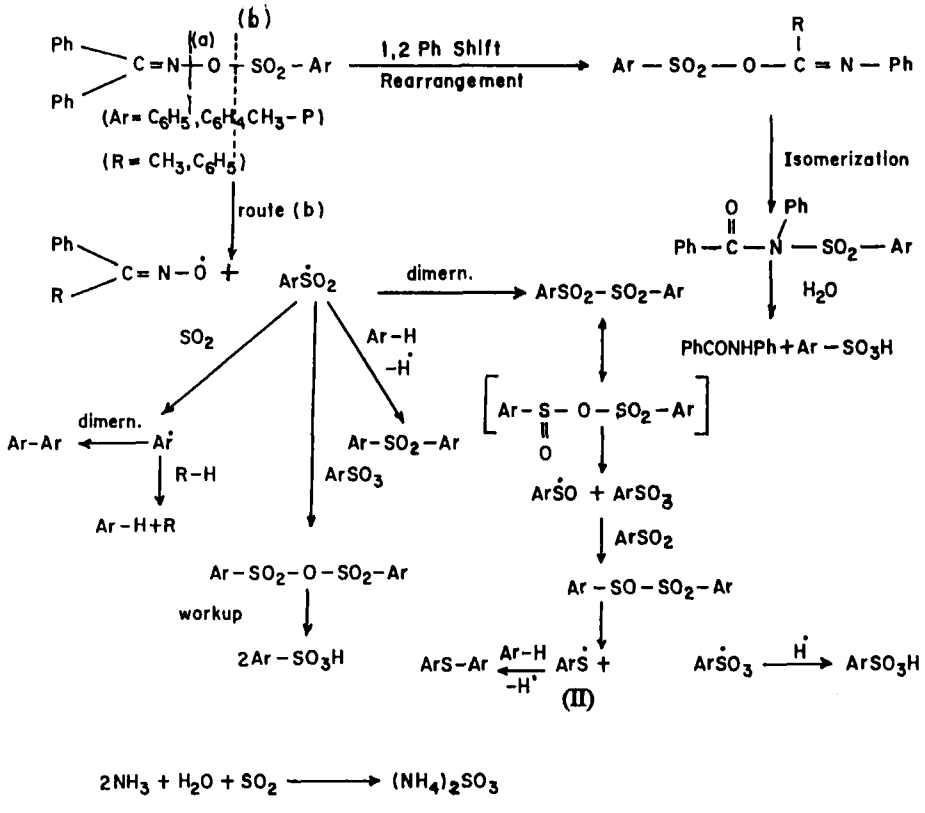
SCHEME (1)

tophenone oxime-O-arene sulfonate rather than its isomer N-methylbenzamide provides strong evidence for the selective migration of phenyl compared with the methyl group. The iminoxyl radical (**II**), may abstract the hydrogen forming unsubstituted oxime which subsequently undergoes homolysis of the (N—O) bond to form iminyl and hydroxyl radicals. The iminoxyl radical may undergo cyclization into benzoxazole derivatives[15] as shown in Scheme (3).

The hydroxyl radicals may substitute on aromatic nuclei through cyclohexadienyl radical intermediate forming phenolic compounds. Similar results were obtained from thermolysis of benzophenone oxime benzenesulfonate (**3**), and/or benzophenone oxime p-toluenesulfonate (**4**). Benzanilide, 2-phenylbenzoxazole and other products normally derived from arene-sulfonyl radicals have been interpreted as previously mentioned in the case of acetophenone oxime arenesulfonates as shown in Table I.

These results showed no clear differentiation in product distribution between the thermolysis of acetophenone oxime benzenesulfonate (**1**) and acetophenone oxime p-toluenesulfonate (**2**) or between benzophenone oxime benzenesulfonate (**3**) and benzophenone oxime p-toluenesulfonate (**4**).

The same was observed for compound (**1**) and (**3**) and for (**2**) and (**4**). However this is anticipated for a free radical mechanism.



SCHEME (2)

TABLE I

Pyrolysis products of ketoxime arenesulfonates

Products in g(%)	Expt. No.			
	1	2	3	4
SO_2	0.4(2)	0.3(1.5)	0.4(2)	0.3(1.5)
NH_3	exist	exist	exist	exist
Arene	1.3(6.5)[a]	1.2(6)[b]	1.2(6)[a]	1.3(6.5)[b]
Biaryl	2.6(13)[C]	2.8(14)[d]	2.5(12.5)[c]	2.7(13.5)[d]
Diaryl sulfide	0.3(1.5)[e]	0.4(2)[f]	0.3(1.5)[e]	0.3(1.5)[f]
Diaryl disulfide	0.6(3)[g]	0.8(4)[h]	0.6(3)[g]	0.6(3)[h]
Diaryl sulfone	1.6(8)[i]	1.5(7.5)[j]	1.6(8)[i]	1.5(7.5)[j]
Diaryl disulfone	0.5(2.5)[k]	-	0.4(2)[k]	-
Aryl amm.sulfonate	0.4(2)[l]	0.4(2)[m]	0.3(1.5)[l]	0.4(2)[m]
Arenesulfonic acid	3.0(15)[n]	3.2(16)[o]	3.3(16.5)[n]	3.2(16)[o]
Ammoniumsulfite	traces[p]	traces	traces	traces
Phenols	1.7(8.5)[q]	1.7(8.5)[r]	1.5(7.5)[q]	1.7(8.5)[r]
Anilides	2.2(11)[s]	2.3(11.5)[t]	2.4(12)[s]	2.3(11.5)[t]
Ketones	2.1(10.5)[u]	2.2(11)[v]	2.3(11.5)[u]	2.4(12)[v]
Nitriles	0.5(2.5)[w]	0.5(2.5)[x]	0.6(3)[w]	0.6(3)[x]
Benzoxazole derivatires	0.2(1)[y]	0.3(1.5)[z]	0.4(2)[y]	0.4(2)[z]

Expt. (1) Pyrolysis of acetophenone oxime benzenesulfonates; (2) pyrolysis of acetophenone Oxime-p-toluenesulfonate; (3) pyrolysis of benzophenone oxime-benzenesulfonate; (4) pyrolysis of benzophenone oxim-p-toluenesulfonate.

[a]Identified by glc.

[b]Toluene identified by glc.

[c]Biphenyl m.p. and mixed m.p. 70°C, dinitroderivative m.p. and m.m.p. 234°C.

[d]P,P-ditolyl m.p. and m.m.p. 125°C.

[e]Diphenyl sulfide m.p. and m.m.p. 57–58°C detected by glc.

[f]Di.p. tolylsulfide m.p. 57.5°C.

[g]Diphenyldisulfide detected by glc, m.p. and m.m.p. 61°C.

[h]Di.p. tolyl disulfide m.p. and m.m.p. 46°C.

[i]Diphenlysulfone m.p. and m.m.p. 124–125°C.

[j]Di.p. tolylsulfone m.p. and m.m.p. 159°C.

[k]Diphenyldisulfone m.p. and m.m.p. 194–96°C.

[l]Phenylammonium sulfonate detected by $BaCl_2.C_6N_9SNO_3$ Found S 18.4. Calc. S 18.2%.

[m]p.tolyl ammonium sulfonate detected by barium chloride.

[n]Benzenesulfonic acid.

[o]p.toluenesulfonic acid.

[p]Ammonium sulfite detected by barium chloride.

[q]Phenol identified by chemical test.[16]

[r]p.cresol identified by chemical test.

[s]Acetanilide m.p. and m.m.p. 114°C; I.R. coincident with that of authentic sample.

[t]Benzanilide m.p. and m.m.p. 163°C; I.R. coincident with that of authentic sample.

[u]Acetophenone D.N.P. derivative m.p. 250°C.

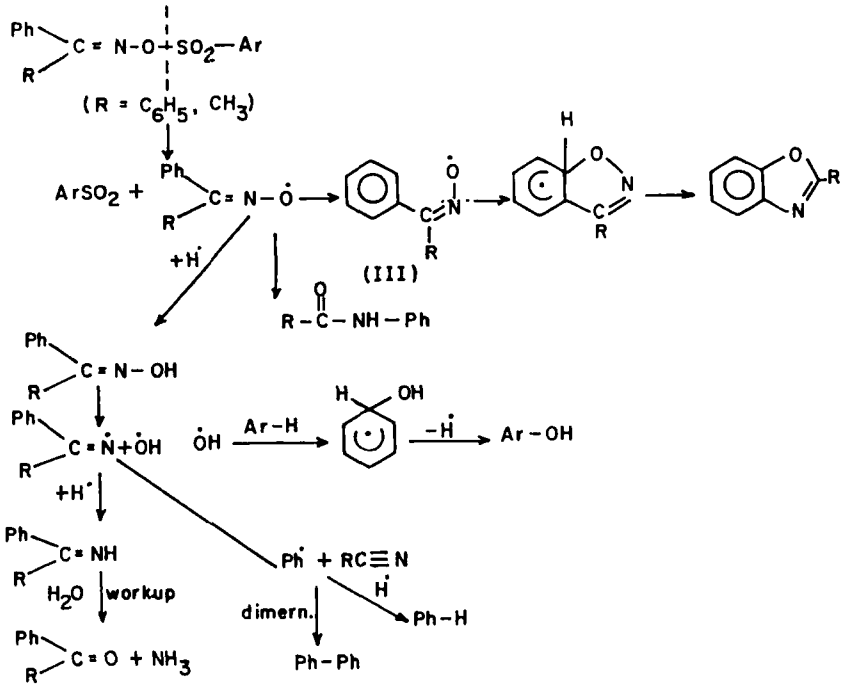
[v]Benzophenone m.p. 49°C, D.N.P. derivative m.p. 23°C.

[w]Acetonitrile $^nD^{20}$ 1.3442 on acid hydrolysis gives acetic acid.

[x]Benzonitrile $^nD^{20}$ 1.5270 on acid hydrolysis gives benzoic acid.

[y]2. Methylbenzoxazole $^nD^{20}$ 1.550′ m/z 133, its I.R. coincident with that of authentic sample.

[z]2. Phenylbenzoxazole m.p. and m.m.p. 101°C, m/z 194 and its I.R. spectrum coincident with that of authentic sample.



SCHEME (3)

TABLE II

Photolysis products of ketoxime arenesulfonates

Products in g(%)	Expt. No.			
	1	2	3	4
SO_2	exist	exist	exist	exist
Biaryl	0.3(15)	0.4(20)	0.3(15)	0.4(20)
Diaryl sulfone	0.4(20)	0.3(15)	0.3(15)	0.4(20)
Arenesulfonic acid	0.8(40)	0.9(45)	0.8(40)	0.9(45)
ketone	0.2(10)	0.2(10)	0.3(15)	0.3(15)
Anilide	0.07(3.5)	0.07(3.5)	0.08(4)	0.08(4)
phenols	0.03(1.5)	0.02(1)	0.01(0.5)	0.02(1)

Expt. (1) photolysis of acetophenone oxime benzenesulfonates; (2) photolysis of acetophenone oxime p.Toluenesulfonate; (3) photolysis of benzophenone oxime benzenesulfonate; (4) photolysis of benzophenone oxime p.toluenesulfonate.

Preparation of reference compounds:

Diphenyl sulfide[17] oil b.p. 115°C/3 mm Hg.

Diphenyl disulfide,[18] crystallized from pet. ether (40–60°C), m.p. 60–61°C.

Diphenyl sulfone,[19] crystallized from ethanol, m.p. 128°C.

Diphenyl disulfone,[20] crystallized from benzene, m.p. 193–95°C.

Di.p. tolyl,[21] crystallized from ethanol m.p. 125°C.

Di.p. tolyl sulfide,[22] crystallized from ethanol m.p. 57–58°C.

Di.p. tolyl disulfide,[23] crystallized from pet. ether (60–80°C), m.p. 46–47°C.

Di.p. tolyl sulfone,[24] crystallized from water, m.p. 159°C.

Di.p. tolyl disulfone,[20] crystallized from benzene m.p. 221°C.

Photolysis of these ketoxime arenesulfonates in acetone at 280 nm at 25°C affords analogous products to those obtained from thermolysis. Hence it is reasonable to assume that the photolysis of these ketoxime arenesulfonate involves the homolysis of (N—O), (S—O) bonds[8,11] (as shown in Schemes (1 and 2)) to give free a radical species which either reacts within the solvent cage affording the rearrangement products or escapes out of the cage to give the fragmentation products shown in Table (II).

EXPERIMENTAL

Melting points were measured with a Gallenkamp apparatus and are uncorrected. Thin-layer chromatography was carried out on glass plates covered with silica gel (25–40 mesh) and eluted with pet.ether Acetone (2:8 v/v). Gas liquid chromatography was carried out on a Perkin Elmer Sigma 3B. Columns used are 1.2 m × 4 mm packed with 30% SE 30 on Chromosorb W (35–80 mesh) or 10% SE 30 on Celite (60–80 mesh) using nitrogen as a carrier gas.

Molecular weight determination of some reaction products was carried out by mass spectrophotometer Model A.E.I.M.S. 902. Ketoxime arenesulfonates were prepared by the standard method in the literature.[3] Ultraviolet irradiation was carried out using a Mallinkrodt 150-W mercury discharge lamp; the solvents were of analytical grade and were used without further purification.

Thermolysis of ketoxime arenesulfonates: The oxime (20 g) was refluxed in tetralin for 2 hrs. The gases evolved were detected by standard chemical means: (SO_2 detected by the benzidine blue test,[16] NH_3 detected by Nessler's reagent. The pyrolysate in tetralin was subjected to fractional vacuum distillation to separate the liquid products. The solid products were dissolved in acetone and filtered to remove the ammonium salts. The filtrate was digested in hot absolute ethanol to dissolve ammonium sulfonate leaving behind the ammonium sulfite. The acetone solution was evaporated to dryness, diluted with water and titrated with standard sodium carbonate solution to estimate the arenesulfonic acid followed by extraction with ether. The ether layer was chromatographed on silica gel (80–120 mesh) and eluted with pet. ether (40–60°) acetone mixture. The separated products were identified by physical constants: bp's, mp's, tlc, glc, IR or MS as compared with authentic samples (cf. Table I).

Photolysis of ketoxime arenesulfonates: Ketoxime sulfonate (2 g) which was dissolved in acetone (100 ml) was irradiated for 10 hrs at room temperature. The free sulfonic acid was estimated with standard sodium bicarbonate. The organic material was extracted with ether, washed, dried and evaporated to dryness. The residue was chromatographed on silica gel using a pet.ether (60–80°C) acetone mixture as eluent, its composition is given in Table (II).

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