

OXIDATION OF SULFENAMIDES

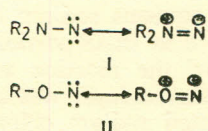
TANWEER AHMAD CHAUDRI*

University of Liverpool, P.O. Box No. 143, Liverpool, L47 3Bx, U.K.

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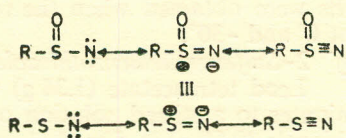
Abstract. Oxidation of *p*-nitrobenzenesulfenamide and 2-sulfenamido benzothiazole was carried out with lead tetraacetate and monochloramine. The expected sulfonylnitrene or bis-(sulfonyl)-diimide were not obtained but the only product obtained in excellent yield was the corresponding disulfide. Oxidation of bis(*p*-toluenesulfonyl) hydrazine did not give the corresponding diimide but instead the disulfone was obtained. The oxidation reactions suggested that sulfonyl group (R—S) is a very good leaving group when a nucleophile attacks.

The oxidation of *N*-amine¹ or *O*-amine² compounds have been reported to give the corresponding nitrenes (I) and (II). The nitrenes have been re-



ported to be relatively stable and selective, possibly existing in the singlet state, which can effectively be stabilized by delocalization and are, most likely in the ground state.

We were interested to see, whether other nitrenes adjacent to suitably filled *p*-orbital can overlap as shown in the case of (I) or (II). The sulfur case is particularly interesting since one can write a fully covalent structure for the sulfinyl (III) and sulfonyl (IV) nitrenes, and the possibility of stabilization of the singlet state of sulfonylnitrene by delocalization of the lone-pair of the sulfur into the vacant nitrogen orbital has been suggested.³

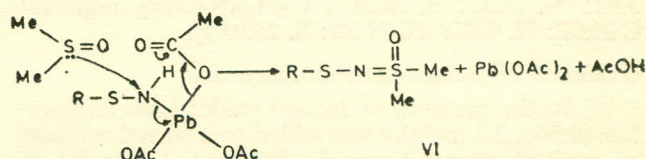
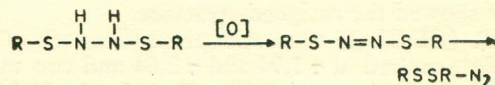
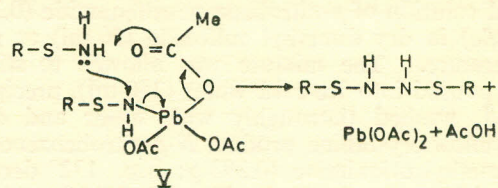


In this paper we report the oxidation of sulfenamides with lead tetraacetate and monochloroamine. The work was carried out with the hope to generate sulfonylnitrene (IV) which possibly has the covalent structure (R—S≡N) and might well be stable enough to be detected by physical or chemical means. Indeed all our attempts to generate and trap such nitrenes have failed altogether.

The oxidation of *p*-nitrobenzene sulfenamide in dry dimethylsulfoxide with lead tetraacetate gave a good yield of *N*-*p*-nitrobenzenesulfonyl dimethylsulfoximine in fairly good yield and it looked as if sulfonyl nitrene (IV) was involved. The results of other experiments mentioned below revealed that no nitrene is formed but the possible formation of

nitrenoid (V) could be postulated. The reaction in mesityl oxide gave a 40% yield of the corresponding disulfide and no nitrene adduct was obtained. Tetraphenylcyclopentadiene was used as a trapping agent for the expected reactive intermediate with a hope to detect possibly fully covalent form of the nitrene (IV). The products isolated were unreacted tetraphenylcyclopentadiene and *p*-nitrobenzene disulfide in 65% yield. The oxidation in the presence of olefines, cyclohexene and norbornylene gave quantitative yield of the corresponding disulfide.

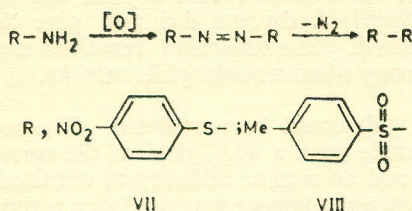
The possible mechanism which could be advanced to account for the sulfenamide-lead tetracetate reaction could be an initial attack by lead tetracetate on sulfenamide to give the nitrenoid intermediate (V). The sulfenamide present in the reaction mixture reacts with the intermediate (V) to give bisulfenylhydrazine and oxidation of the bisulfenylhydrazine could give rise to diimide which in turn with the loss of nitrogen will give rise to disulfide. The formation of the sulfoximine (VI) could be explained by the scheme given below:



Lead tetraacetate is a strong oxidizing agent, therefore, we decided to look into some milder agent for the oxidation. Monochloroamine has been reported to react with aliphatic amine to give corresponding hydrazine⁴ while the primary aromatic amines under these conditions are oxidized to corresponding azo-

*Now at the PCSIR Laboratories, Ferozepur Road, Lahore.

benzenes.⁵ Extensive work on the monochloramine as aminating agent and oxidizing agent has been reported in the literature and recently Jaffari and Nunn⁵ have reported that primary aromatic amines treated with monochloramine under mild conditions gave the corresponding azobenzenes, both as *cis* and *trans*-isomers. The experiment was designed to oxidize *p*-nitrobenzene sulfenamide with monochloramine with a hope to form the bis(*p*-nitrobenzenesulphenyl)-diimide (VIII).



The attempts were unsuccessful although the reaction temperature was lowered to -30° and the products obtained in quantitative yield were ammonium chloride and disulfide. Most probably the diimide (VII) was formed as an intermediate which with the loss of nitrogen gave disulfide.

We attempted to prepare bis(*p*-nitrobenzenesulphenyl) hydrazine so as to generate diimide (VII) but without any success and instead decided to check that the formation of (VIII), if plausible, by bis(*p*-toluenesulfonyl)hydrazine⁶ oxidation. The corresponding diimide was found very unstable and the only product isolated was di-*p*-toluene-disulfone.

Experimental

N-*p*-Nitrobenzenesulphenyldimethylsulfoximine. Lead tetraacetate (0.93 g; 2.1 mmole) was added to a stirred solution of *p*-nitrobenzenesulfenamide (0.34 g; 2mmole) in dry dimethyl sulfoxide (30 ml) at room temperature. The mixture was allowed to stir for 1 hr, poured into ice-cold water (250 ml), precipitate filtered, washed thoroughly with water and dried. The yellow crystalline product *N-p*-nitrobenzenesulphenyldimethylsulfoximine (0.393 g; m.p. 132° decomp; 79% yield) was obtained. The IR, NMR and mass spectra showed the assigned structure.

NMR (CDCl₃), aromatic protons as set of two multiplets centred at τ 1.94 and τ 2.64 and two methyl groups as singlet at τ 6.80. Found; C, 39.26; H, 3.92; N, 11.32; S, 26.31%. C₈H₁₀N₂O₃S₂ requires: C 39.02; H, 4.07; N, 11.38; S, 25.01%.

Oxidation of *p*-Nitrobenzenesulfenamide

(a) In the presence of mesityl oxide: Lead tetraacetate (0.96g, 2.2 mmole) was added to a stirred solution of *p*-nitrobenzenesulfenamide (0.34 g; 2 mmole) in mesityl oxide (40 ml) at 20°C and was stirred for one hr, after which temperature was allowed to rise slowly (1 hr) and stirring was continued further for 1 hr. The precipitate was filtered and found to be polymeric material, while the filtrate gave *p*-nitrobenzenedisulfide (0.123g; m.p., 181° , 40% yield).

(b) In the presence of tetraphenylcyclopentadiene: The reaction was carried out as mentioned above at

room temperature in dry methylene chloride and the residue obtained from the reaction was absorbed on silica and eluted with benzene (yield: tetraphenylcyclopentadiene 45%; and *p*-nitrobenzenedisulfide 65%).

(c) In the presence of norbornylene: The reaction was carried in the same manner as described above (b), in the presence of norbornylene, *p*-nitrobenzenedisulfide was obtained in 88% yield and norbornylene recovered quantitatively.

(d) In the presence of cyclohexene: The reaction was carried out as mentioned in (b) in the presence of cyclohexene and *p*-nitrobenzenedisulfide was obtained in 86% yield.

Ethereal monochloramine. Chloramine was prepared by a modification of method of Coleman and Hauser.⁶ To cooled (-10°) suspension of powdered ammonium chloride (13.5 g) in ether aqueous ammonia (33%, 30 ml) was added. The mixture was vigorously stirred and aqueous sodium hypochlorite (140 ml, 1.6 M) was added in small portions during 10 min. The temperature of the reaction mixture was kept below -10° . The ethereal layer was separated, washed once with a saturated sodium chloride solution and dried (CaCl₂) for 1 hr at -15° . An aliquot was assayed iodometrically; ether was evaporated before the mixture was titrated with thiosulphate. The ethereal chloramine solution was in the range of 0.1–0.2M.

Reaction of *p*-Nitrobenzenesulfenamide with Monochloramine. *p*-Nitrobenzenesulfenamide (200 mg) was dissolved in dry methylene chloride (10 ml) and to that monochloramine in ether (100 ml) vast excess was added at room temperature, white precipitate was formed after about 2 hr, but the reaction mixture was stirred overnight. The white precipitate was filtered, dried and found to be ammonium chloride (0.0623 g; 99%) and *p*-nitrobenzenedisulfide (0.165 g; m.p., 181° , 91%) was obtained from the solvent.

Same results were obtained when the reaction was carried out at 0° and -30° .

Reaction of 2-Sulfenamidothiazole with Lead Tetraacetate. Lead tetraacetate (1.38 g) was added in about 2 minutes to a stirred solution of 2-sulfenamidothiazole (0.55 g) in dimethyl sulfoxide (25 ml). The reaction mixture was allowed to stir for 2 hr poured into ice water, precipitate filtered, dried and crystallized from benzene. Benzethiazole-2-disulfide (0.093 g, m.p., $176-77^\circ$; 10%) was obtained along with a large amount of polymeric material.

N,N'-Di-*p*-toluenesulfonylhydrazine. To a solution of *p*-toluenesulfonylhydrazine (7.44 g, 40 mmole) in dry pyridine (100 ml) *p*-toluenesulfonyl chloride (7.62 g, 40 mmole) was added at room temperature. After a few minutes white crystalline compound started coming out of the reaction mixture, which was stirred for 2 hr. The solvent was evaporated under vacuum and the crystalline residue filtered and washed with dilute hydrochloric acid followed by water and dried. N,N'-Di-*p*-toluenesulfonylhydrazine⁷ (9.56 g, m.p. $219-200^\circ$ decomp. 100%), was obtained.

Oxidation of N,N'-di-*p*-toluenesulfonylhydrazine. To a solution of N,N'-di-*p*-toluenesulfonylhydrazine (0.68 g) in acetonitrile (150 ml) lead tetraacetate

(0.93 g) was added and the gas evolution took place very quickly. The mixture was stirred, filtered, the filtrate was evaporated and the residue was taken into methylene chloride. The solution was washed with water, dried (MgSO_4), solvent evaporated and white crystalline compound from methylene chloride, di-*p*-toluenedisulphone (0.346 g, m.p. 280° , 56% lit. m.p. 210°) was obtained.

References

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