

Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol. 18, Nos. 1-2, February-April, 1975

OXIDATION OF SULPHONAMIDES WITH LEAD TETRAACETATE

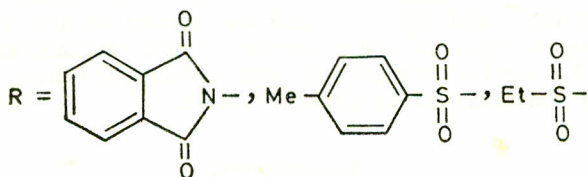
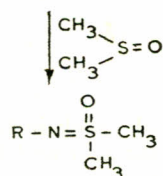
TANWEER A. CHAUDRI

PCSIR Laboratories, Lahore 16

(Received May 2, 1974; revised November 7, 1974)

Abstract. *p*-Toluenesulphonamide on treatment with lead tetraacetate in dimethylsulphoxide gave sulphoxamine in excellent yield, while in the presence of sulphides gave sulphilimine. No adduct was obtained on treatment of *p*-toluenesulphonamide with lead tetraacetate in presence of norbornylene, cyclohexene and tetracyclone. The reactions do not proceed via sulphonylnitrenes.

Sulphoximines and sulphilimines have been synthesised by thermal reaction of Chloramine-T with dimethylsulphoxide either in presence or absence of copper.¹ Two recent communications have given the synthesis of sulphoximine from *N*-amino compounds² and sulyhonamides³ by oxidation with lead tetraacetate. It has been suggested that the corresponding nitrene was generated by oxidation.



Sulphonamides have been regarded as completely inert towards lead tetraacetate,⁴ but recently Ohashi and his coworkers³ have suggested that oxidation of sulphonamides by lead tetraacetate proceeds to give sulphonyl nitrenes. Our work revealed that the sulphonamides are inert towards lead tetraacetate oxidation.

Attempts were made to oxidise *p*-toluenesulphonamide with lead tetraacetate in presence of dimethylsulphoxide, methyl phenyl sulphide, dimethyl sulphide, norbornylene, cyclohexene and tetracyclone. Sulphoximines and sulphilimines were obtained in the first three cases while in the latter cases, sulphonamide was recovered unreacted. The results are summarised in Table 1.

Horner and Christmann⁵ were the first to photolyze sulphonylazide in sulphoxide and sulphide solvents the products obtained being *N*-sulphonylsulphoxi-

TABLE 1

Trapping agent	Adduct and yield %	Unreacted sulphonamide
(CH ₃) ₂ S=O	$R-N=\overset{\text{O}}{\underset{\text{CH}_3}{\text{S}}}-\text{CH}_3$ 89	—
CH ₃ -S-CH ₃	$R-N=\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{S}}}$ 52	—
CH ₃ -S-C ₆ H ₅	$R-N=\overset{\text{CH}_3}{\underset{\text{C}_6\text{H}_5}{\text{S}}}$ 50	—
Norbornylene	Nil	Quantitative
Cyclohexene	"	"
Tetracyclone	"	"

mines (I) and *N*-sulphonylsulphilimines (II) respectively. Similar results have been reported⁵ in the thermal decomposition of sulphonylazide.

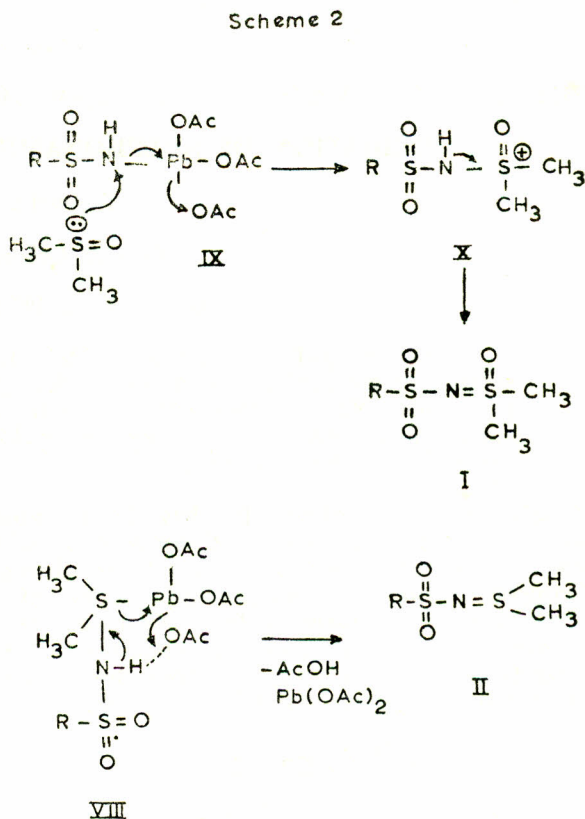
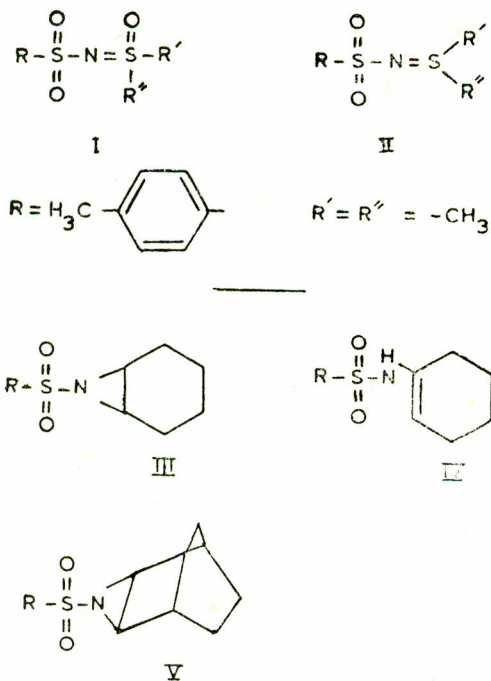
Metal-catalysed decomposition of sulphonylazide has been reported^{6,7} to give the corresponding sulphoximines. These reactions proceeded with retention of configuration, as would be expected of attack by nitrenes.

Kwart and Khan⁶ investigated the copper-catalysed decomposition in cyclohexene; a bewildering variety of products were formed, chief among them being sulphonamide, aziridine (III), an enamine (IV) and cyclohexanone. Decomposition in the presence of norbornylene⁸ has been shown to produce aziridine (V).

In the light of our results and keeping all the literature in view, it is suggested that the oxidation of sulphonamides with lead tetraacetate did not proceed via sulphonyl nitrenes. The two possible reaction mechanisms are discussed:

1. Initial attack of lead tetraacetate on sulphoxide to give the intermediate (VI).

Sulphonamide present in the solution attacks the sulphur cation to give intermediate (VII) which in turn rearranges to sulphoximine (I) acetic acid and lead acetate. In the case of sulphide, intermediate



(VIII) is formed which in turn rearranges to sulphilimine (II), acetic acid and lead acetate.

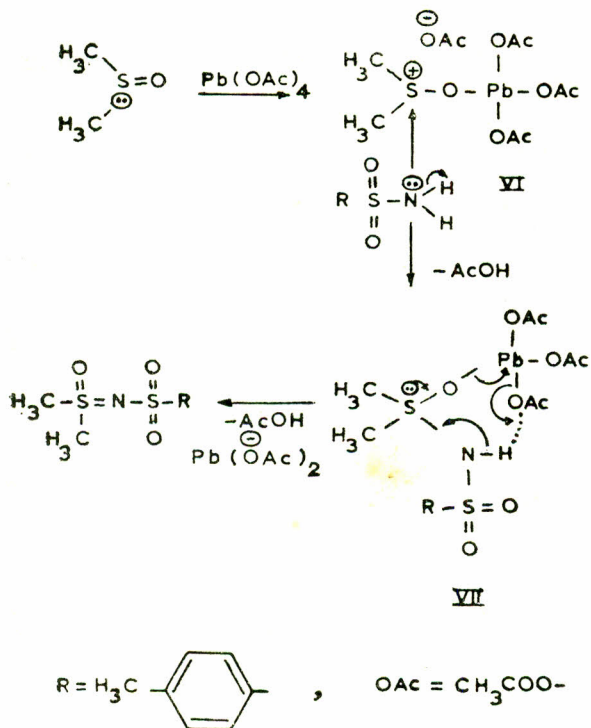
2. The second possible route could be explained by the initial attack of lead tetraacetate on the nitrogen centre of sulphonamide to give intermediate (IX), which in turn gives the intermediate (X) followed by rearrangement to sulphoximine(I).

Experimental

N-p-Toluenesulphonyldimethylsulphoximine. Lead tetraacetate (4.89 g, 11 mmole) was added in over 2 min to a stirred solution of *p*-toluenesulphonamide (1.71 g, 10 mmole) in dimethylsulphoxide (30 ml) at room temperature. The reaction mixture was stirred for 1 hr then poured into ice-cold water (200 ml). The white crystalline product was filtered and dried. *N-p*-Toluenesulphonyldimethylsulphoximine (2.19 g, 89%; m.p. 169–170°, lit. m.p. 169–170°). The IR, NMR and mass spectra were identical to an authentic sample prepared from *p*-toluenesulphonylazide and dimethylsulphoxide.

NMR (CDCl_3), τ 2.16 (*d* 2H); τ 2.76 (*d* 2H); τ 6.66 (*s* 3H) and τ 7.61 (*s*, 3H).

N-p-Toluenesulphonylmethylphenylsulphilimine. *p*-Toluenesulphonamide (1.71 g, 10 mmole) and phenylmethylsulphide (6.28 g, 50.5 mmole) were dissolved in ether (200 ml) and lead tetraacetate (4.89 g, 11 mmole) was added with vigorous stirring at room temperature.



The reaction mixture very quickly gave a yellow suspension which gradually changed to a white precipitate in about 1½ hr. The solvent was evaporated and the residue washed with water, dried and crystallized from ethanol. Sulphilimine (1.48 g, 50%; m.p. 128–130° d) was obtained as white cubes. $C_{14}H_{15}NO_2S_2$

NMR ($CDCl_3$) τ 2.87 (m 9H); τ 7.16 (s 3H) and τ 7.65 (s 3H).

Found: C, 57.05; H, 5.19; N, 4.70; S, 21.80.

Requires: C, 57.33; H, 5.12; N, 4.77; S, 21.84%.

$C_{14}H_{15}NO_2S_2$.

N-p-Toluenesulphonyldimethylsulphilimine. Lead tetraacetate (4.89 g, 11 mmole) was added in about 2 min to a stirred solution of *p*-toluenesulphonamide (1.71 g, 10 mmole) and dimethylsulphide (6.4 g, 0.1 mole) in ether (200 ml) at room temperature. A yellow precipitate was formed immediately which gradually changed to white precipitate in about 1½ hr. The solvent was evaporated under vacuum, the residue washed with water, dried and crystallized from ethanol as white needles (1.21 g, 52%, m.p. 160–161°; lit. m.p. 159°).

NMR ($CDCl_3$), τ 2.26 (*d* 2H), τ 2.78 (*d* 2H), τ 7.33 (*s* 6H) and τ 7.63 (*s* 3H).

Attempted Reaction in Presence of Norbornylene, Cyclohexene and Tetracyclone. Lead tetraacetate (4.89 g, 11 mmole) was added in over 2 min to a stirred solution of *p*-toluenesulphonamide (1.71 g, 10 mmole) and norbornylene (4.8 g, 30 mmole) in dry methylene chloride (100 ml). The reaction mixture was stirred for 4 hr, washed with water, dried ($MgSO_4$) and solvent evaporated under vacuum. The residue was treated with light petroleum, *p*-toluenesulphonamide was filtered in quantitative yield and norbornylene was recovered from light petroleum mixture.

Similar results were obtained when reactions were carried out in presence of cyclohexene or tetracyclone using methylene chloride or ether as solvents.

Acknowledgement. The author is thankful to Professor C.W. Rees for helpful discussion. Thanks are also due to analysis and NMR spectra services of University of Liverpool, England.

References

1. (a) D. Carr, T.P. Seden and R.W. Turner, *Tetrahedron Letters*, 477 (1969); (b) A. Schonberg, E. Singer, *Chem. Ber.*, **102**, 2557 (1969).
2. D.J. Anderson, T.L. Gilchrist, D. C. Horwell and C.W. Rees, *Chem. Commun.*, 146 (1969).
3. T. Ohashi, K. Matsunaga, M. Okabora and O. Komori, *Syn.*, 96 (1971).
4. R.A. Abramovitch, *Quart Rept. Sulfur Chem.*, **3**, 1 (1968).
5. L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).
6. (a) H. Kwart and A.A. Khan, *J. Am. Chem. Soc.*, **89**, 1950 (1967); (b) H. Kwart and A.A. Khan, *ibid.*, **89**, 1951 (1967).
7. M.A. Sabol, R.W. Davenport and K.K. Andersen *Tetrahedron Letters*, 2159 (1968).
8. (a) J.E. Franz and C. Osuch, *Tetrahedron Letters*, 837 (1963); (b) J. E. Franz, C. Osuch and M.W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964); (c) L.H. Zalkow, A.C. Oehlschlager, G. A. Cabat and R.L. Hale, *Chem. Ind. (London)*, 1556 (1964).
9. R. A. Abramovitch, C. I. Azogu and I. T. McMaster, *J. Am. Chem. Soc.*, **91**, 1219 (1969).