Tetrahedron Letters No.10, pp. 729-732, 1971. Pergamon Press. Printed in Great Britain.

# THE REACTION OF ARENESULFINYL AZIDES WITH DIMETHYL SULFOXIDE.

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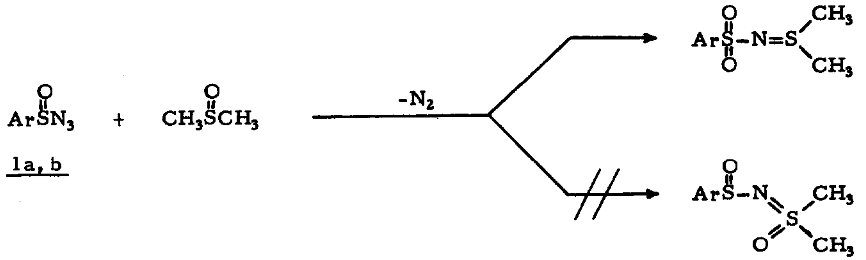
(Received in USA 2 February 1971; received in UK for publication 16 February 1971)

We wish to report the first case where an acyl azide (or nitrene) -DMSO reaction product is not a sulfoximine, but rather a sulfilimine. The reaction of arenesulfinyl azides (1) with DMSO[1] affords arenesulfonyl sulfilimines (3) and is consistent with the intermediacy of a delocalized, "nucleophilic nitrene" (2).



1a, b

3

4

a b

Ar = $C_6H_5$- p-$CH_3C_6H_4$-

Decomposition of 1[2] in acetonitrile solution containing from one to two equivalents of DMSO gave the usual nitrogen evolution (*ca.* 85% based on sulfinyl chloride) and afforded the respective N-arenesulfonyl dimethylsulfilimine (3) in up to 70% yield (45% recrystallized). At O° with a moderate rate of nitrogen evolution (half-life *ca.* 50 min) the yield of 3 was about 25%, but increased substantially upon rapid decomposition of 1 at or above 25°.

The sulfilimines (3) were prepared by an independent procedure[4] and were shown by their infrared spectra and mixed melting points to be identical to the sulfinyl azide products. The previously unknown sulfoximines 4 have been prepared by the reaction of arenesulfinyl chloride with N-lithio dimethylsulfoximine[5] (ca. 45% yield) or the N-sodio derivative[6] (ca. 70% yield). Instrumental methods (ms, ir, and nmr) were definitive in assigning structures, which were confirmed by chemical degradation.

We have shown that 4 cannot be an intermediate in the sulfinyl azide - DMSO reaction. When the sulfinyl azide (1a or b) was allowed to decompose in the presence of DMSO and the same or differently labeled sulfoximine (4a or b), only the labeled sulfoximine which was added was recovered (up to 80%), and only the sulfilimine (3a or b) having the label of the azide was isolated. Therefore 4 doesnot rearrange to 3 under the reaction conditions.

Because of a rate dependence on added DMSO, Kwart and Kahn[7] proposed an intermediate cycloadduct between p-toluenesulfonyl azide and DMSO, which could afford the sulfonyl sulfoximine product on loss of nitrogen. An intermediate benzenesulfinyl azide - DMSO adduct (like 5) may be excluded in our system, however, because first order kinetics

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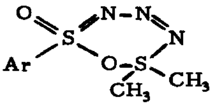
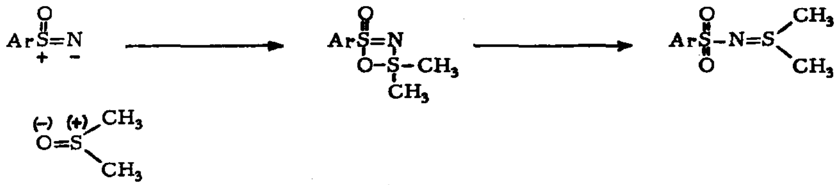


(to 90% reaction) and similar rate constants were observed whether DMSO was present or not. The rate constant for nitrogen evolution at 0° in acetonitrile in the absence of DMSO was $3.0 \times 10^{-4}$ sec$^{-1}$. Under similar reaction conditions with 2.5 to 3 equivalents of DMSO added, the rate constant was ca. $2.2 \times 10^{-4}$ sec$^{-1}$. The slight difference in rates may be due to a solvent effect.

In the light of these results, we favor a mechanism in which a dipolar sulfinyl nitrene intermediate (2) reacts directly with DMSO to give 6, which then rearranges to 3.



2 6 3

The reaction mechanism might have involved deoxygenation of DMSO by 2 to give sulfonyl nitrene and methyl sulfide, which could recombine to give 3. However, considering the availability of DMSO, failure to isolate arenesulfonyl dimethylsulfoximines from these reactions argue against the sulfonyl nitrene intermediate or at most for a highly competitive recombination with methyl sulfide.

Acknowledgements: This investigation was supported in part by a Frederick Gardner Cottrell grant from Research Corporation. We wish to acknowledge the skillful laboratory assistance of R. Wong and V. Munson.

## REFERENCES

(1) In a preliminary study [T. J. Maricich, J. Am. Chem. Soc, 90, 7179 (1968)] of the chemistry of benzenesulfinyl azide (1a), we failed to isolate the product from reaction with DMSO.

(2) Benzenesulfinyl azide (1a) was prepared essentially as reported earlier[1], but with the exclusion of added agents such as sodium iodide and pyridine. It appears that such agents are unnecessary and undersirable; rather, special care in purifying the reagents and solvent are sufficient. The azide solutions are almost colorless, instead of the red-orange color obtained with added sodium iodide. Added pyridine produced complicating changes in the kinetic order and rate of azide decomposition. Toluenesulfinyl azide (1b) was synthesized similarly without difficulty below -35°. The lower stability of 1b is likely responsible for the failure of other investigators to isolate it.[3]

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