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OXIDATION OF 1,2-*bis*-(BENZENESULFONYL)HYDRAZINE TO 1,2-DIPHENYLDISULFONE

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Abstract: *The oxidation of 1,2-bis(benzenesulfonyl)hydrazine yields diphenyldisulfone and* ***not*** *1,2-bis(benzenesulfonyl)dimide as previously reported.*

Diethyl azodicarboxylate (**DEAD**),[1] one of the earliest dienophiles utilized by Diels,[2] has acquired renewed importance as one of the key components of the *Mitsunobu* reaction.[3] This latter reaction is undergoing rapid expansion as evidenced by the unending flow of applications in the current literature. It has been established that the "acid-base" type interaction between **DEAD** and the phosphines is an essential step in the Mitsunobu reaction and it was thought that *azodisufonyls* (ADS)[4] such as 1,2-*bis*-(benzenesulfonyl)diimide (**2**) might serve as even more reactive substitutes for **DEAD**. In 1968, Kwart and Khan described the preparation and isolation of **2** (no yield) as a stable, crystalline - presumably colorless - solid, mp. 193-194°C (with fuming and decomposition).[5] On the other hand, Bock had earlier reported, in a review,[6] that attempts to generate **2** had resulted in decomposition, even at temperatures as low as -50°C; to our knowledge, the details of this latter work have not been published. In spite of this daunting report, it was thought that the availability of a stable and readily prepared substitute[7] for **DEAD** warranted further investigation.

Unfortunately, several attempts to duplicate the procedure, which involves oxidation of 1,2-*bis*-(benzenesulfonyl)hydrazine (**1**)[5] in ethanol at reflux with a very large excess (*nearly 100 fold*) of bromine, have so far failed; no identifiable solid could be isolated. In a further attempt to obtain **2**, compound **1** was treated with sodium hypochlorite at 0-5°C. Gas evolution was observed almost immediately and eventually a colorless, crystalline solid was isolated in 41% yield. Its mp. 193-195°C (dec.) matched that reported for **2**.[5] Its infrared spectrum displayed a peak of moderate intensity at 1575 cm^{-1}. However, much to our surprise, the combustion analysis detected *less than 0.2% of nitrogen.* A repurified sample gave results which corresponded to $C_{12}H_{10}O_4S_2$; the mp. of diphenyldisulfone (**3**) is reported to be 193-194°C. Indeed a comparison of the product obtained with that of an authentic sample of **3**[8] matched in every respect. Its

$$\underset{\mathbf{2}}{\mathbf{PhSO_2N{=}NSO_2Ph}} \xleftarrow[\text{EtOH}]{\text{Br}_2,\ \Delta} \underset{\mathbf{1}}{\mathbf{PhSO_2NHNHSO_2Ph}} \xrightarrow[\text{CHCl}_3]{\text{NaOCl}} \underset{\mathbf{3}}{\mathbf{PhSO_2SO_2Ph}}$$

Raman spectrum exhibited a peak at 1576 cm^{-1} and its UV spectrum was transparent above 300 nm.[9] So far, we are able to account for all the data (including the ^1H nmr) reported for the putative **2** as belonging to the disulfone **3**.[10] For example, the reported[5] mass spectrum showed no parent peak at *m/e* 310. One of the stronger peaks of the mass spectrum of

the presumed **2** was ascribed to the disulfone **3**, supposedly arising by loss of nitrogen from **2**. The most prominent peak at *m/e* 141 was assigned to the $PhSO_2^+$ fragment. Curiously, a peak at *m/e* 171 was ascribed to the $PhSO_2NHNH^+$ fragment, the source of these hydrogens being left unidentified. This peak was observed in the mass spectrum of the starting hydrazine **1** as well as unpurified samples of **3**. However, one piece of the data[5] that we cannot rationalize is the combustion analysis which lists 8.97% of nitrogen! This value and those of the other elements (including a reported *oxygen* analysis), are beyond any resonable limits of even an impure sample of **3**. We are unable to account for this glaring discrepancy.[11]

In conclusion, we believe that the product isolated by Kwart and Khan to be diphenyldisulfone, arising most likely by extrusion of elemental nitrogen from the transient diimide **2**,[6] followed by coupling of the benzenesulfonyl radicals.

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2. Diels, O. ; Blom; J. H.; Koll,W. *Ann.*, **1925**, *443*, 242.
3. Hughes, D. L. *Org. React.*, **1992**, *34*, 335.
4. "*Azodisulfonyls*" is a generic term which we are using in analogy to "*azodicarbonyls*" (see reference 1).
5. Kwart, H.; Khan, A. A. *J. Org. Chem.*, **1968**, *33*, 1537.
6. Bock, H. *Angew. Chem. Int. Eng. Ed.*, **1965**, *4*, 458, 460.
7. Compare with the preparation of **DEAD** [*Org. Syn.*, **1955**, *Coll. Vol. 3*, 375; **1963**, *Coll. Vol. 4*, 411] and cautions about its explosive decomposition when it is overheated.
8. Kohler, E. P.; MacDonald, M. B. *Am. Chem. J.*, **1899**, *22*, 219.
9. Surprisingly, no UV data, a commonly used criterion for azo compounds, was reported for **2**.
10. Houben-Weyl's *Methoden der Organischen Chemie*, **1955**, *IX*, 254 ; 1985, *E11*,1121.
11. Unfortunately, Prof. Kwart has passed away and we were unable to obtain any data of the original work.

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