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

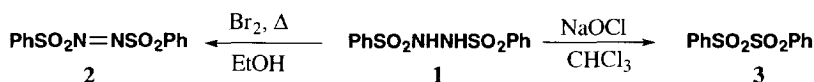
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Abstract: *The oxidation of 1,2-bis(benzenesulfonyl)hydrazine yields diphenyldisulfone and not 1,2-bis(benzenesulfonyl)diimide as previously reported.*

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 *azodisulfonyls* (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 substitute⁷ 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 C₁₂H₁₀O₄S₂; 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



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 reported⁵ 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 $\text{PhSO}_2\text{NHNH}^+$ 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 data⁵ 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 reasonable 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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† Pfizer Inc. Fellow, 1994.

1. Moody, C. J. in *Advances in Heterocyclic Chemistry*, Katritzky, A. R., Ed., Academic Press, New York, NY, Vol. **21**, 1 (1982).
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, *EII*, 1121.
11. Unfortunately, Prof. Kwart has passed away and we were unable to obtain any data of the original work.

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