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CONVERGENCE OF MECHANISMS BETWEEN SULFINYL AZIDE AND N-ALKOXYSULFINAMIDE REACTIONS[1]

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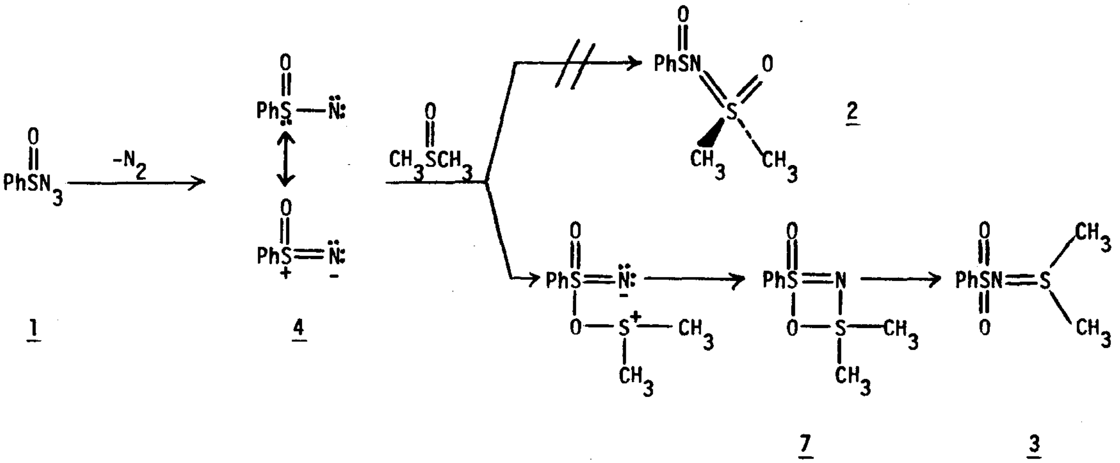
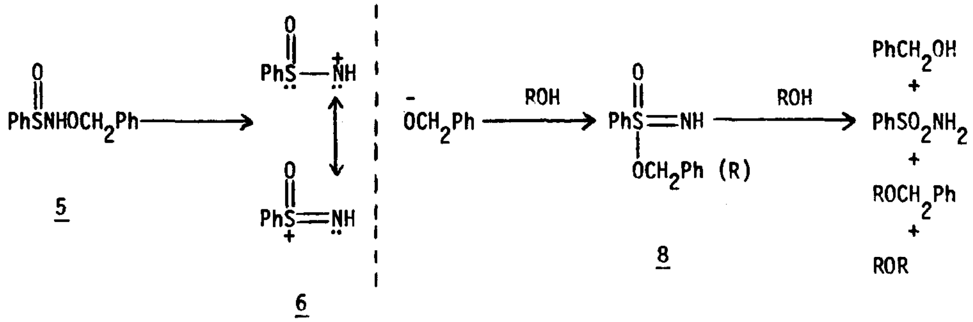
We recently reported[2] that the reactions of benzenesulfinyl azide (1) with sulfoxides gave abnormal adducts compared with other azides.[3-6] Instead of a normal sulfoximide (2) adduct,[3-6] we obtained N-benzenesulfonyl sulfimides (3)[2]. The results support a two-step 1,2-dipolar cycloaddition of a delocalized sulfinylnitrene intermediate (4) with sulfoxide, followed by ring opening.[2]



In another study[7], we reported that certain N-alkoxybenzenesulfinamides (5) reacted with alcohols in a way that implicated a sulfinylnitrenium ion intermediate (6).

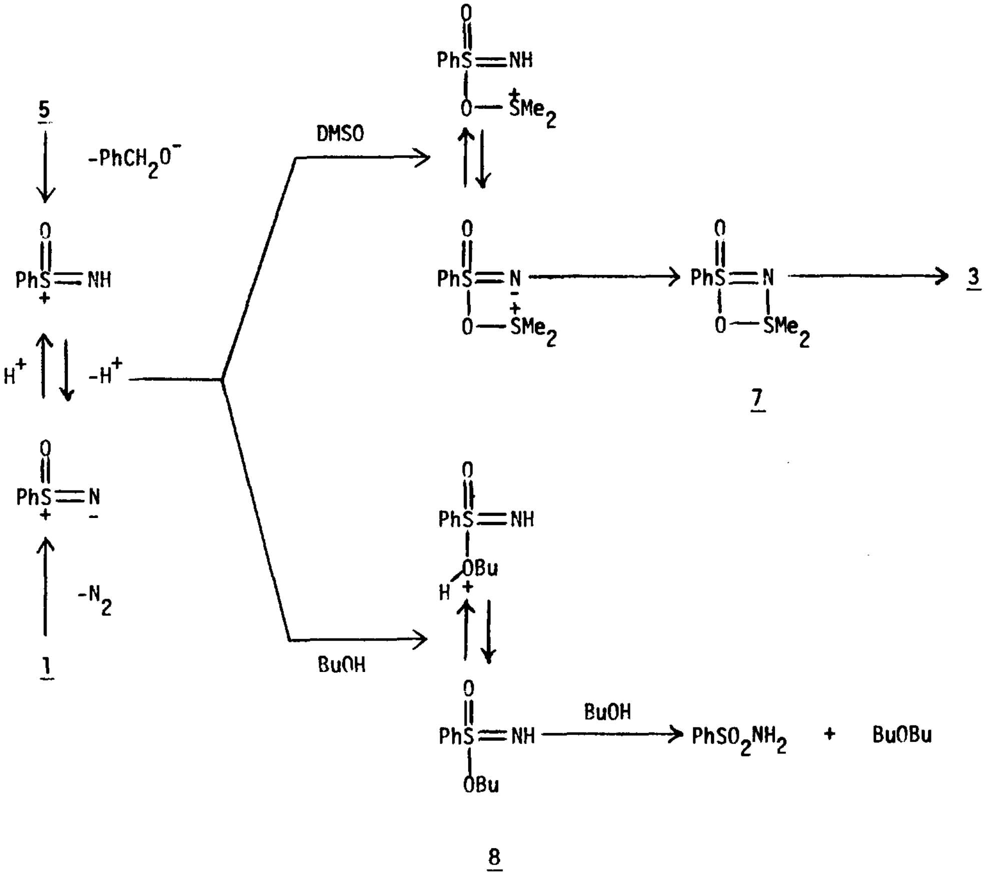


We now wish to report evidence supporting the convergence of mechanisms between the sulfinyl azide and N-alkoxysulfinamide reactions with both sulfoxides and alcohols. The major products previously obtained from the reaction of sulfoxides with sulfinyl azides are now also obtained with N-alkoxysulfinamides. Likewise, major products previously obtained from the reaction of alcohols with N-alkoxysulfinamides are now also obtained with sulfinyl azides.

Reaction of 5 with DMSO gave 3, benzenesulfonamide, and benzyl alcohol as the major products. In a typical run, 0.55 g (2.2 mmoles) of 5 and 0.8 ml (11.0 mmoles) of DMSO were heated in an oil bath at *ca.* 42° for 72 hours. The reaction mixture was then extracted with methylene chloride, washed with brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was resolved by dry-column chromatography on silica gel using methylene chloride as developing solvent. Two of the eight spots visible by quenching of the fluorescent indicator were isolated. N-Benzenesulfonyl-S,S-dimethylsulfimide (3) (0.13g, 27.2% yield) and benzenesulfonamide (0.18g, 51.8% yield) were identified by comparing their tlc R_f values, melting points, and infrared spectra with authentic samples. Benzyl alcohol was isolated and identified in a separate run of the same experiment.

Reaction of 1 with n-butanol gave di-n-butyl ether and benzenesulfonamide as principal products. In a typical run, benzenesulfinyl azide (1), prepared from 12.9 mmoles of benzenesulfinyl chloride in cold acetonitrile[2], evolved nitrogen (85% of theory) upon decomposition in the presence of a ten-fold excess of n-butanol at room temperature. Di-n-butyl ether was formed in 55% yield (analysis by glc on carbowax at 140°) and benzenesulfonamide in 25% isolated yield (by dry-column chromotography on silica gel with chloroform). The same ether was obtained upon reaction with p-toluenesulfinyl azide. Products were identified by glc or hplc retention times and ir spectra.

Reactions of 1 and 5 with sulfoxides and alcohols may or may not involve prior equilibration of the sulfinylnitrene and sulfinylnitrenium ion, since proton transfer could readily occur after reaction of the nucleophile with the reactive intermediate.



Thus, whatever the case, the reactions of 1 and 5 with DMSO must converge at the cyclic sulfurane (7) leading to sulfimide (3); and reaction with n-butanol must converge at the sulfonimidate (8), leading to sulfonamide and di-n-butyl ether.

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