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ON PHENYLSULFINYL CARBENIUM ION

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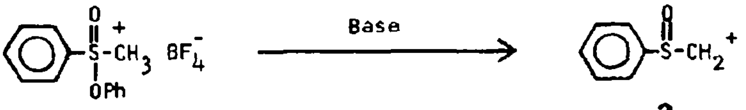
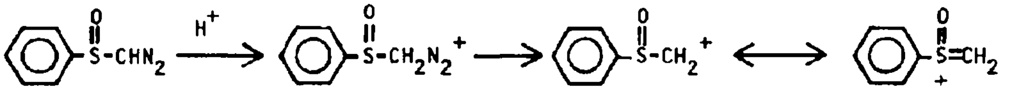
SUMMARY: Phenylsulfinyl carbenium ion, generated by the acid-catalyzed decomposition of phenyl diazomethyl sulfoxide or the silver-assisted solvolysis of phenyl iodomethyl sulfoxide, is trapped by hydroxylic solvents to yield phenyl methyl sulfone. The possibility of the intermediacy of either phenylsulfinyl carbene or phenylsulfinylmethyl acetate has been ruled out.

The recent reports of Oishi[2] and Still[3] that phenyl methyl phenoxy oxosulfonium tetrafluoroborate (1) reacts with bases in ways best explained by the intermediacy of phenylsulfinyl carbenium ion, 2, prompts us to report in preliminary form our own attempts to purposefully generate 2. We were led to postulate the likelihood of a more stable than expected sulfinyl carbenium ion after we found that phenylsulfinyl carbene is unusually stable due to the abilit of the sulfinyl function to donate its lone electron pair to an adjacent empty orbital with facility[4].



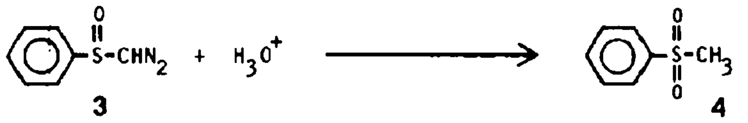
1 2 (1)

Phenyl diazomethyl sulfoxide[5] seemed a likely source of the carbenium ion by decomposition of its conjugate acid diazonium ion as shown in equation 2. Because the diazo sulfoxide decomposes to phenylsulfinyl carbene with a half-lif of 50 minutes at 0°C[6], the acid-catalyzed decomposition must be carried out quickly. When phenyl diazomethyl sulfoxide was dripped into stirring 8:1:1 $CH_3CN:H_2O:HO_2CCH_3$ at 0°C, and the products worked up by concentrating in vacuo, dissolving in ether, washing with saturated $NaHCO_3$ and H_2O, drying over $MgSO_4$,



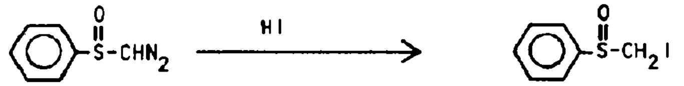
3 2 (2)

and removing the ether in vacuo, phenyl methyl sulfone (ca. 80% conversion) was identified as the major product derived from the diazo compound, equation 3.



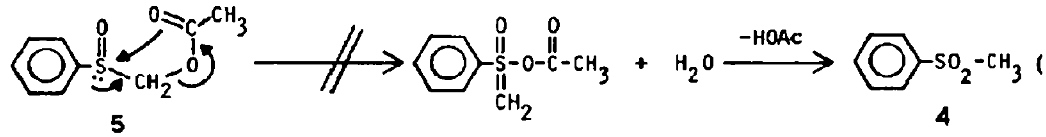
(3)

That the product under these acid-catalyzed conditions does not arise by the thermal decomposition of 3 to phenylsulfinyl carbene and subsequent reaction of the carbene with H_2O, can be inferred from two experiments. First, phenyl methyl sulfone (4) is not found among the products when acetic acid is omitted from the solvent mixture and the reaction otherwise run the same way. Secondly, quenching of the reaction mixture with 48% HI at a time insufficient for the loss of 3 via the known thermal decomposition gave no phenyl iodomethyl sulfoxide confirming that the diazo sulfoxide had been destroyed by a route other than carbene formation. Phenyl diazomethyl sulfoxide is known to react rapidly with 48% HI to give phenyl iodomethyl sulfoxide[5].



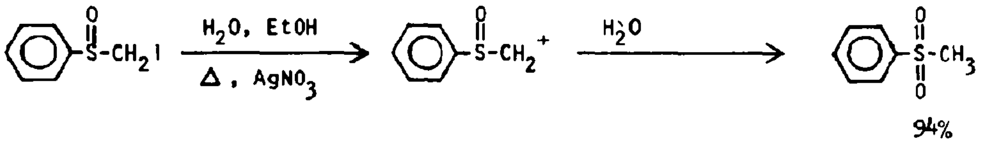
(4)

The observation of the cine-substitution, in which the sulfur appears to be oxidized and the adjacent carbon reduced, is itself reason to postulate the carbenium intermediate. If an S_N2 reaction of the initially formed diazonium ion took place, one would expect to observe α-functionalized sulfoxides or their decomposition products rather than the sulfone. Phenyl hydroxymethyl sulfoxide would be expected to fragment to formaldehyde and benzenesulfenic acid[7], for example. The possibility that phenylsulfinylmethyl acetate, 5, is formed and is an intermediate in the formation of 4, equation 5, has been ruled out because authentic 5[8] is stable to the reaction conditions.



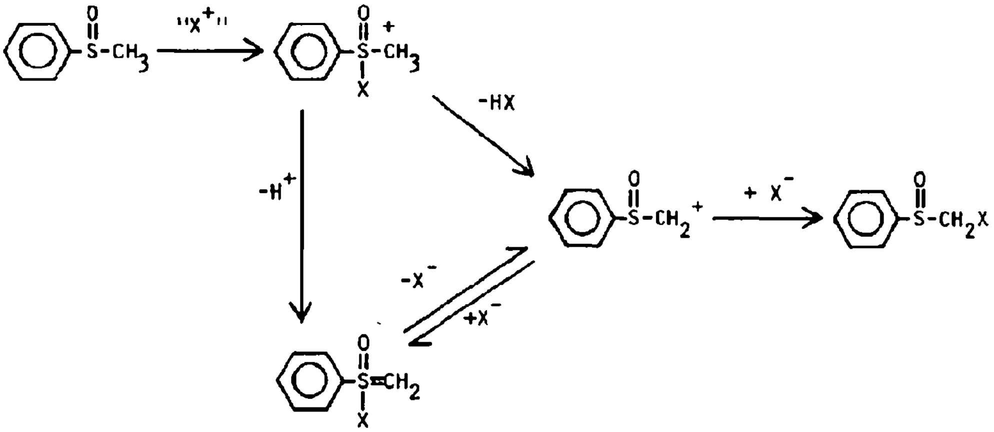
(5)

One way to test the intermediacy of the phenylsulfinyl carbenium ion is to attempt its generation from a different precursor. Therefore, we have solvolyzed phenyl iodomethyl sulfoxide[9] (6) in the presence of silver nitrate. The product is again phenyl methyl sulfone, further substantiating the postulation of the existence of phenylsulfinyl carbenium ion, equation 6.



(6)

The existence and unexpected stability of a sulfinyl carbenium ion has profound implications for the long controversy over the mechanism of the α-halogenation of sulfoxides[9]. A scheme involving reversible halide attack at the sulfur of the electrophically ambident sulfinyl carbenium ion competing with irreversibl attack at carbon, can account for all of the facts known about the halogenation. Thus, the observation of sulfinyl carbenium ions in other systems lends additional support to the α-halogenation mechanism proposed by Durst[10], Marquet[11], and Klein[12], Scheme 1.



SCHEME 1 PROPOSED MECHANISM FOR SULFOXIDE α-HALOGENATION

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