with the proposed mechanism. This reaction shows no buffer catalysis and has the rate law, k_m [RSH][RS$^-$][flavin], consistent with a breakdown step analogous to k_{10} in Scheme I being rate determining. Breakdown from an N(5) adduct is inconsistent with these results, because the reaction should then be buffer catalyzed, as discussed above. The breakdown step with dithiols is faster because of proximity effect.[19]

The attack of a thiol anion at C(4a) is analogous to the attack of thiols on imines, a reaction for which there is chemical precedent.[20] Breakdown of adduct III is somewhat analogous to the reaction of thiols with thiocyanate,[21] and the leaving group (reduced flavin anion) is similar to an anionic enamine. Thiol attack at C(4a) with general acid catalaysis at N(5) is analogous to the general acid catalyzed attack of sulfite on C(4a).[22]

We have demonstrated that an oxidation-reduction reaction of flavins with dithiols proceeds by way of a covalent intermediate. This reaction may serve as a model for lipoic acid dehydrogenase, thioredoxin, and glutathione reductase.

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(5) Steps k_3 and k_6 in Scheme I could represent specific acid catalysis if the pK for protonated N(5) in I were greater than about −2. Steps k_4 and k_7 could represent stepwise thiol addition at C(4a) followed by diffusion controlled protonation by water at N(5) if pK of N(5) in II or III were less than about 24. These possibilities are under investigation.
(6) Below pH 7 in a range where breakdown is 50% or more rate determining there is a transition from one buffer term to another. This new term could represent either general acid catalysis at N(1) in breakdown (below the pK_a of N(1) in reduced I) or general base catalyzed removal of a sulfur proton from II.
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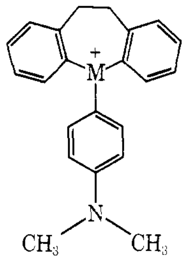
Generation of a Silicenium Ion in Solution[1]

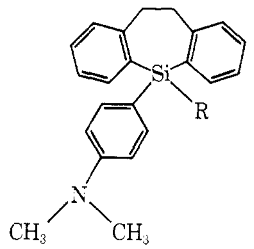
Sir:

Five-coordinate siliconium ions have been reported in salts such as $[(C_6H_5)_3Si(2,2'\text{-bipy})]I$[2] and $[SiH_3(2,2'\text{-bipy})]Co(CO)_4$[3] but no definitive examples of the generation of a trivalent silicenium ion in solution or in the solid state have yet been reported. Although carbenium ions have been studied by physicochemical methods, have been prepared as salts, and are widely accepted intermediates in organic chemistry, the literature contains a number of reports describing unsuccessful attempts to demonstrate the formation of R_3Si^+ in solution by methods that have proved useful in carbenium ion chemistry.[4,5]

The carbenium ion model chosen for the present study was the moisture and air stable carbocation **1b.**[7] The value of pK_{R^+} for **1b** is at least 11 orders of magnitude greater than that of triphenylcarbenium ion ($pK_{R^+} = -6.6$), which is a commonly used and convenient hydride abstraction reagent.[8]



1a, M = Si
b, M = C



2a, R = H
b, R = D
c, R = OH

The silane precursor **2a** of the silicenium ion **1a** was readily prepared in 54% yield by the reaction of *o,o'*-dilithiobibenzyl with *p*-dimethylaminophenyldichlorosilane.[9] The silane **2a** was purified by recrystallization from heptane to give a solid: mp 100–101.5°; NMR (CCl_4, δ relative to TMS) 7.7–6.55 (m, 11.8, aromatics), 5.5 (s, 0.87, SiH), 3.17 (s, 4.12, $-CH_2CH_2-$), 2.87 (s, 6.17, NMe_2); ir (CCl_4) 2118 cm^{-1} (SiH); *m/e* (70 eV) 329.

Reaction of 0.71 g (2.16×10^{-3} mol) of silepin **2a** with 0.74 g (2.16×10^{-3} mol) of triphenylcarbenium perchlorate in methylene chloride (25 ml)[10] at −40 to −50° generates a yellow-green solution. Rapid addition of this solution to a cold solution of $NaBD_4$ in dry diglyme resulted in an instantaneous discharge of color. After removal of the solvents at 30° under vacuum, the residue was dissolved in CH_2Cl_2 and filtered to remove excess $NaBD_4$, and the organic layer was hydrolyzed with water. The products were separated by column chromatography (silica gel) using hexanes-benzene as eluant. Triphenylmethane was obtained in 83% yield and the silepin **2b** was obtained in 70% yield: mp 101–102°; NMR ($CDCl_3$, δ relative to TMS), 7.8–6.6 (multiplet, 11.9, aromatics), 3.2 (s, 4.28, $-CH_2CH_2-$), 2.87 (s, 5.80, NMe_2); *m/e* (70 eV) 330. The deuterated silepin **2b** may contain a trace of starting silepin **2a** as indicated by a very weak residual ir absorption at 2118 cm^{-1}.[12] A similar trapping experiment with a slurry of $NaBH_4$ in wet dioxane afforded triphenylmethane, silepin **2a**, and silanol **2c**, in 81, 36, and 62% yields, respectively.

When the cold yellow-green reaction mixture was allowed to warm to room temperature, brilliant blue-green solutions were produced. Although triphenylmethane can be isolated in 75–88% yields from the room-temperature reactions, treatment of the remaining blue, solid, silicon-containing materials with either $NaBH_4$, $NaBD_4$, or H_2O did not afford products identifiable with the starting silepin skeleton.

The results of the trapping reactions are consistent with and provide prima facie evidence for the generation of a silicenium ion in methylene chloride at low temperatures. Previous attempts to chemically trap silicenium ions were not successful.[4,13] Work is in progress to clarify further the nature of the yellow-green intermediate.

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Phenyl Diazomethyl Sulfoxide (Phenylsulfinyldiazomethane) and Phenylsulfinyl Carbene, a Highly Stereoselective Cyclopropanating Agent[1]

Sir:

Although both sulfenyl[2,3] and sulfonyl[2,4] carbenes are well-characterized intermediates which have been known for some time, the corresponding sulfinyl carbenes are unknown. This deficit arises because the anions of α-halo sulfoxides apparently do not expel halide[5] and because α-diazo sulfoxides[6] and one class of reasonable precursors, α-amino sulfoxides,[9] are unknown. Another class of possible precursors, α-oxo sulfoxides (thiolester *S*-oxides), are known only as unstable reaction intermediates.[10] We wish to report the preparation of the first characterized α-diazo sulfoxide and its facile conversion into phenylsulfinyl carbene, a highly stereoselective cyclopropanating agent.

$$CH_2N_2 + PhS(O)Cl \rightarrow \underset{\mathbf{1}}{PhS(O)CH_2Cl} + \underset{\mathbf{2}}{PhS(O)CHN_2}$$

Addition of benzenesulfinyl chloride to excess diazomethane in THF at −78° gave, after removal of solvent, an oily mixture of phenyl chloromethyl sulfoxide (**1**) and what we believe to be phenyl diazomethyl sulfoxide (phenylsulfinyldiazomethane) (**2**) based on the following observations. The infrared spectrum of the mixture showed a strong band at 2040 cm^{-1} which was not in the spectrum of pure **1**. Although α-diazo ketones[11] and α-diazo sulfones[12] absorb near 2100 cm^{-1}, this shift from the normal diazoalkane frequency of 2040 cm^{-1} is usually attributed to the acidifying effect of the carbonyl or sulfonyl group, an effect which would not be nearly as strong in the case of the sulfinyl group. The NMR of the mixture shows a band at δ 5.5 which is not found in **1**. This chemical shift is in the region expected from analogy to α-diazo sulfones[12] and other diazoalkanes.[13]

$$R_2C{=}N_2 + HA \rightarrow R_2CHA + N_2$$

Further evidence for the diazo sulfoxide structure derives from the chemistry of this new compound. One of the characteristic reactions of the diazo group is its facile replacement by strong acids.[14] When the crude mixture of **1** and **2** is treated with excess hydrochloric acid, **1** can be isolated in a quantitative yield based on starting benzenesulfinyl chloride. Similar treatment with hydrobromic acid gives a 64:36 mixture of phenyl bromomethyl sulfoxide and **1** as estimated by NMR, while hydriodic acid reacts to give 65% phenyl iodomethyl sulfoxide[15] and 35% **1**. Control experiments show that **1** is not converted into the iodomethyl compound under the reaction conditions. Thus, the initial product of addition of benzenesulfinyl chloride to CH_2N_2 in THF is a 2:1 mixture of phenyl diazomethyl sulfoxide (**2**) and phenyl chloromethyl sulfoxide (**1**).

An important and characteristic reaction of diazo compounds is their ability to cyclopropanate olefins.[2] Addition of cooled tetrahydrofuran solutions of mixtures of **1** and **2** to room temperature cyclohexene or *E*- or *Z*-2-butene at 0° gave phenylsulfinyl cyclopropanes in 35–40% isolated yields based on starting benzenesulfinyl chloride. Typically, 35–40% of **1** was also isolated, further confirming the approximately 2:1 ratio of **2** to **1** estimated from HX quenching experiments. The stereospecificity of the cyclopropanation was checked with the 2-butenes.[16] *E*-2-Butene gave cyclopropanes with >97% of the methyl groups trans, and *Z*-2-butene gave cyclopropanes with >99% of the methyl groups cis. The reaction appears to be a singlet carbene cycloaddition. The possibility that the reaction occurs by a two-step mechanism involving the formation and decomposition of a Δ^1- pyrazoline, while unlikely at the low temperatures of these reactions, has been considered. One might expect that a pyrazoline (probably Δ^2-3-phenylsulfinyl-pyrazoline) would be isolable under the reaction conditions by analogy to sulfonylpyrazolines.[17] However, none has been found. To test the nature of the intermediate further, we have allowed a 1:1 mixture of cyclohexene and diethyl fumarate to react with **2**. Recently, Houk and coworkers have presented a general perturbation molecular orbital treatment of 1,3 dipolar cycloadditions.[18,19] Their predictions are in accord with the experimental observations that substituted styrenes as dipolarophiles with diazomethane show a $\rho = +0.90$[20] and that dimethyl fumarate is 1750 times more reactive than styrene as a dipolarophile with diphenyl diazomethane[21] and that, in general, olefins with electron-withdrawing substitutents are superior 1,3-dipolarophiles with diazoalkanes. On the basis of these observations and calculations, one can confidently predict that diethyl fumarate should be much more reactive with **2** than should be cyclohexene, *if* the reaction is a 1,3-dipolar addition. When a 1:1 mixture of diethyl fumarate and cyclohexene is allowed to react with **2,** no adducts of diethyl fumarate with either **2** or phenylsulfinyl carbene are found. In fact, although the yield of norcaranes is reduced from 50 to 30% as estimated from NMR, they are definitely still the major products even in