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 the presence of the added diethyl fumarate.[22] The stereoselectivity of phenylsulfinyl carbene was determined in its addition to both Z-2-butene and cyclohexene. The ratio of anti addition to syn addition,[23] anti/syn, is 34/1 for addition to cyclohexene and >99/1 for addition to Z-2-butene. Compared to the stereoselectivities of other carbenes, these ratios are extremely large.[25-27]

Hoffman, Levin, and Moss,[28] on the basis of extended Huckel calculations, state that "in highly exothermic association reactions, where the transition state occurs at large separation of reaction partners, the activation energy for the path leading to the sterically more hindered product may be lower." They suggest that this may be the explanation for the contrathermodynamic syn stereoselectivity exhibited in the addition of many unsymmetrical carbenes to olefins. Although the data for benzenesulfinyl carbene seem to be contrary to their postulations, a closer examination reveals that the stereoselectivity data for sulfenyl, sulfinyl, and sulfonyl substituted carbenes provide a basis for further refinement of their theory.

The phenylsulfinyl substituent is large (A value of 1.9[29]) but the observation of a high degree of anti stereoselectivity is not simply a steric effect, since the sterically larger phenylsulfonyl group (A value of 2.5[30]) imparts no such selectivity to phenylsulfonyl carbene (anti/syn = 2.1 for addition to cyclohexene[31]). Electronically, the phenylsulfinyl substituent can stabilize the carbene center by delocalization of its lone pair into the empty orbital on carbon whereas the phenylsulfonyl substituent cannot.[32] Increased stability should lead to a more product-like transition state and to a higher degree of anti stereoselectivity. On the other hand, phenylsulfenyl carbene, though stable, is relatively nonstereoselective (anti/syn = 0.77 for addition to cyclohexene[24]). We believe that this lack of discrimination is due to the small steric size of the phenylsulfenyl group (A value of 0.8[34]). Thus, it appears that a substituent must be *both stabilizing and large* if it is to direct a high degree of anti stereoselectivity.

Further studies of diazo sulfoxides and sulfinyl carbenes are underway.

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A Highly Activated Cyclopropane for Homoconjugate Reactions

Sir:

In contrast to double bonds, which are susceptible to the Michael reaction[1] by virtue of one activating group (eq 1, X = CO_2R, CN, etc), cyclopropanes require two such activating groups for homoconjugate addition. The process formalized in eq 2 for nucleophiles has been reported for enolates,[2a-c] amines,[3] mercaptans,[3] enamines,[4] and cuprates.[5] However, the severity of the conditions usually required for the intermolecular process even with two activating groups[6-8] has sharply reduced its attraction as a synthetic method.[9-13]

We considered the case of compound **1** in which both activating groups are esters, the most widely studied system in