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STERIC AND ELECTRONIC FACTORS IN THE ADDITION OF PHENYLSULFINYL CARBENE TO METHYL-SUBSTITUTED ETHYLENES.

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The unusual stability of phenylsulfinyl carbene, signalled by (1) the ease by which it is formed unimolecularly from phenyl diazomethyl sulfoxide, (2) the lack of C-H insertion reactions, and (3) the high degree of stereoselectivity in cycloaddition to Z-2-butene and cyclohexene,[2] strongly suggests that the sulfinyl sulfur can stabilize the carbene by donation of its lone electron pair into the empty orbital of the carbenic carbon, a conclusion at odds with the generally held view that the sulfinyl function is an electron-withdrawing group.[3] Since Moss[4] has proposed that just such a donation (σ_R^+) is quite important in the correlation of relative rate data for the addition of a number of carbenes to a series of methyl-substituted ethylenes, we have determined the relative rates of addition of phenylsulfinyl carbene to the same set of alkenes. The results support both our contention that the sulfinyl function can be a good electron donor and the general applicability of Moss's carbene reactivity numbers, m_{CXY}, to the understanding of carbene reactivities.

The relative rates were determined by the competitive method. Ten mmol of benzenesulfinyl chloride in 10 mL of THF were added dropwise at 25°C to a stirred solution of accurately weighed samples of a pair of alkenes and 25 mmol of CH_2N_2 in 15 to 20 mL of THF. At 25°C the phenylsulfinyl diazomethane formed in situ decomposes ($t_{\frac{1}{2}}$ = ca 3-4 minutes[5]) to the carbene which cyclopropanates the alkenes After the addition of the benzenesulfinyl chloride is complete the mixture is allowed to stir an additional 30 minutes. Quantitative analysis of the product ratios was conveniently carried out by C-13 nmr on the crude reaction mixture after carefully stripping the solvent. The results, along with comparable results for CCl_2, are presented in Table I.

Table I. Relative Reactivities in Carbene-Alkene Addition at 25°C.[6]

	PhS(O)CH		CCl_2
Alkene	Observed Rate[a]	Electronic Rate[b]	Observed Rate[c]
$Me_2C{=}CMe_2$	0.94	3.29	8.98
$Me_2C{=}CHMe$	0.81[d](3.50)	1.26	3.12
$Me_2C{=}CH_2$	1.00	1.00	1.00
cis-MeHC=CHMe	1.05[e](12.1)	0.56	0.27
trans-MeHC=CHMe	0.34	0.34	0.18

[a] Numbers in parentheses are anti-PhS(O)/syn-PhS(O). [b] Electronic rates figured with a steric factor of 3.50. [c] CCl_2 rates from ref. 7. [d] The relative rate for trimethylethylene is the sum of the relative rates of production of syn-(0.18) and anti-(0.63) 2,2,3-trimethyl-1-phenylsulfinylcyclopropanes. [e] The relative rate for Z-2-butene is the sum of the relative rates of production of syn-(0.08) and anti-(0.97) 2,3-dimethyl-1-phenylsulfinylcyclopropanes.

The interpretation of the data was hampered by a large apparently steric effect. Note that whereas tetramethylethylene is the most reactive alkene with CCl_2, the relative rates for addition of phenylsulfinyl carbene go through a maximum at Z-2-butene. In order to compare the phenylsulfinyl carbene reactivities to those previously determined for other carbenes by Moss, it was necessary to separate the steric and electronic effects.

Fortunately, the steric effect can be estimated from the ratio of the syn and anti cyclopropanes obtained when phenylsulfinyl carbene adds to trimethylethylene, since the electronic effect in the two transition states derived from a single precursor should be very nearly the same. The cycloaddition of phenylsulfinyl carbene is 3.50 times faster to the side of trimethylethylene with one methyl than to the side with two methyls. Therefore, to compare only the electronic effects with isobutene, which has only one methyl on each side, one must multiply rates of addition which require interaction with two methyls by 3.50. Hence, the "electronic relative rate" for tetramethylethylene is 0.94 x 3.50 = 3.29. Only the rate for the two methyl side of trimethylethylene requires a steric correction; therefore, its "electronic relative rate" is 0.63 + 3.50(0.18) = 1.26. Z-2-Butene has one side with two methyls and the rate for that side should be multiplied by 3.50. The side leading to the anti-phenylsulfinyl cyclopropane has no methyls, so, approximately, the rate of formation of that product is divided by 3.50. Thus, the "electronic relative rate" for Z-2-butene is 0.97/3.50 + 3.50(0.08) = 0.56. Since both sides of E-2-butene have only one methyl as does isobutene, there is no correction to its relative rate. The degree of correlation (correlation coefficient = 0.976) of these "electronic relative rates" with the relative rates for CCl_2 is gratifying.[8]

The slope of the line, $m_{PhS(O)CH}$, is 0.51. Thus, phenylsulfinyl carbene is about as selective as methylchlorocarbene and nearly as selective as dibromocarbene! If one uses the generally accepted value of σ_I for the methylsulfinyl group of 0.50[9] and the equation relating m_{CXY} to σ_I and σ_R^+ derived by Moss[4] (equation 1),

$$m_{CXY} = -1.10 \left[\sigma_R^+ (X) + \sigma_R^+ (Y)\right] + 0.53 \left[\sigma_I(X) + \sigma_I(Y)\right] - 0.31 \qquad (1)$$

one calculates a σ_R^+ for the phenylsulfinyl substituent of -0.50. This powerful electron donating ability of the phenylsulfinyl substituent is not without precedent. Although his data set is not large, Ricci[10] found that diphenyl sulfoxide was chlorinated under "neutral" conditions 46 times faster than benzene (per ring). The regression equation for that reaction is given in equation 2. Again, assuming a value of 0.50 for σ_I, σ_R^+ (PhS(O)) is calculated to be -0.61.

$$\log \frac{k}{k_0} = -12.2\sigma_I - 13.9\sigma_R^+ \qquad (2)$$

While additional investigation of the resonance donating ability of the sulfinyl function will be needed to finally define the best value for σ_R^+(RSO), these estimates should not be far from the mark. This means that, under conditions of high electron demand, when direct resonance donation of the sulfinyl lone electron pair is possible (σ_R^+ cases), the sulfinyl function can supply electrons by resonance with a facility intermediate between that of sulfenyl sulfur (σ_R^+ = -.55 to -.95)[9] and chlorine (σ_R^+ = -.38) or bromine (σ_R^+ = -.30)[9].

In conclusion, we have confirmed the unusual stability of phenylsulfinyl carbene postulated earlier on circumstantial evidence. This stability arises both by inductive electron withdrawal and the hitherto little recognized ability of the sulfinyl function to substantially stabilize empty orbitals by direct electron donation. In addition, we have shown that it is possible to meaningfully use Moss's carbene reactivity numbers even in cases where steric effects are substantial.

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