Tetrahedron Letters Vol. 21, pp 1509 - 1510 0040-4039/80/0415-1509 \$02.00/0

ELECTROPHILICITY AND NUCLEOPHILICITY IN SINGLET CARBENES.

II. ELECTROPHILIC SELECTIVITY.

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Abstract. *The electrophilic selectivity of the singlet carbene in the addition reaction to olefines is expressed as the derivative of the interaction energy with respect to the ionization potential of the olefine. Theoretically derived reactivity indices agree with experimentally measured selectivities.*

The electrophilicity and nucleophilicity of singlet carbenes in the addition reaction to olefines can be recast in terms of one-electron perturbation theory[1]. Here we present a correlation between experimentally measured and theoretically derived reactivity indices.

The selectivity of a singlet carbene $:CX_1X_2$ is usually determined[2] by measuring the relative addition rates towards a standard set of different olefines. In the framework of the previously derived theoretical model[1], a change in the olefine (propene, butene etc.) corresponds to a raising or lowering of the π (π^*) orbitals of the olefine (ethylene) by the amount Δ (Figure 1). On this basis, selectivity indices S can be defined as,

$$(1) \qquad S = \frac{\partial(\delta E)}{\partial\Delta} = \frac{\partial}{\partial\Delta}(\delta E_{I1} + \delta E_{I2}), \qquad E_\pi = E_\pi + \Delta \ ; \ E_\pi{}^* = E_\pi{}^* + \Delta$$

We have performed a linear regression analysis between experimentally[2] and theoretically[3] determined (Δ =0.) selectivity indices (Table 1), r^2=0.9911.

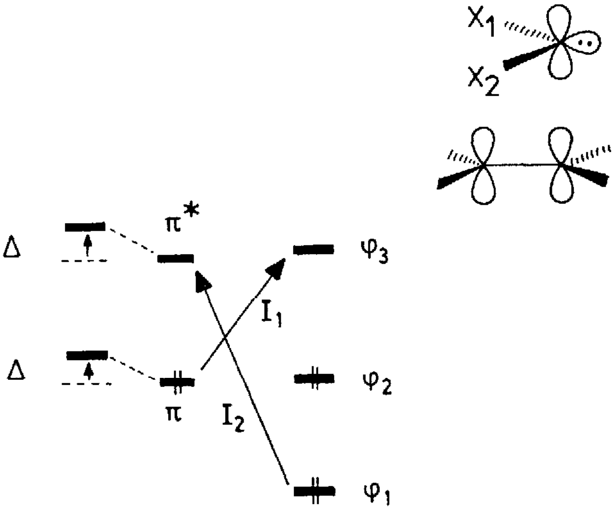
Although the agreement is satisfactory for the halocarbenes, it is not for the phenyl-halo-carbenes[4]. Diamino- , dihydroxy-carbene and cyclopropylidene possess very high selectivity indices. This agrees with cyclopropylidene' preference to behave as a nucleophilic rather than an electrophilic carbene.

Acknowledgement. I thank Professors H.H. Jaffé and G.W. Klumpp for fruitful discussions.

Table 1.

σ^2-carbene	$m_{exp.}$[a]	$m_{calc.}$
$:CF_2$	1.48	1.48
$:CClF$	1.28	1.25
$:CCl_2$	1.00	0.98
$:CBr_2$	0.82[b]	0.84
$:CCH_3Cl$	0.50	0.59[c]
$:CH_2$	0.10[b]	0.05
$:CHF$		0.95
$:CHCl$		0.59
$:CHBr$		0.50
$:CBrF$		1.20
$:CBrCl$		0.91
$:C\Phi F$	0.89	1.59 (0.95)[d]
$:C\Phi Cl$	0.83	1.43 (0.59)[d]
$:C\Phi Br$	0.70	1.40 (0.50)[d]
$:C(NH_2)_2$		2.85
$:C(OH)_2$	2.7[e]	2.56
		2.75

Figure 1.



[a] taken from ref. 2b; [b] taken from ref. 2c; [c] methyl group neglected as π-center; [d] phenyl group twisted by 90 degrees; [e] estimated from Figure 2 in R.A. Moss, M. Vezza, W. Guo, R.C. Munjal, K.N. Houk and R.D. Rondan, J.Amer.Chem.Soc., 101, 5088 (1979).

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(1) W.W. Schoeller, Tetrahedron Letters, preceding communication.

(2) (a) P.S. Skell and M. Cholod, J.Amer.Chem.Soc., 91, 7131 (1969);
(b) R.A. Moss, C.B. Mallon and C.-T. Ho, ibid., 99, 4105 (1977);
(c) C. Wentrup, "Reaktive Zwischenstufen I", Thieme Verlag, Stuttgart 1979.

(3) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", John-Wiley & Sons, Inc., New York 1961, pp. 135; the used parameter values for the computation of the Hückel energies (coefficients) are listed there. For the unsymmetrical carbenes ($X_1 \neq X_2$) the charge transfer from φ_2 to π^* was added. For the fit the first six values of Table 1 were considered.

(4) The theoretically derived m-values for the phenyl-halo-carbenes are a function of the torsional angle of the phenyl group out of the π-system ($\Delta m = m_o (1-\cos\Theta)$).

(Received in Germany 14 December 1979)