Towards a Classification of Singlet Carbenes

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Olefines, Singlet Carbenes

According to one-electron perturbation theory singlet carbenes can be classified as (a) electrophilic, (b) nucleophilic or (c) ambiphilic in their addition properties towards olefines. The nucleophilicity of the σ-orbital in $:CX_1X_2$ should increase with decreasing electronegativity of X_1 (X_2).

The addition of a singlet ground state carbene to olefines can be viewed in terms of one-electron perturbation theory by two types of interactions of the participating orbitals [1]. For the simplest case, σ^2-methylene plus ethylene, this is illustrated in Figure 1.

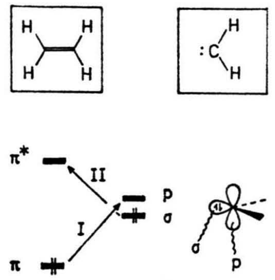


Fig. 1. Orbital interaction diagram for the formation of a π-complex between σ^2-methylene and ethylene.

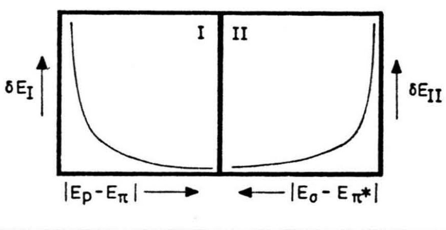
Transfer of electron density can occur from (a) the HOMO π of the olefin to the empty p-AO of the methylene (type I interaction) and (b) the σ-orbital (of the methylene) into the LUMO π^* (type II interaction) [2]. In this respect the singlet carbene can act as an electrophilic ($\pi \rightarrow p$) and/or nucleophilic ($\sigma \rightarrow \pi^*$) species.

The energy profit due to interaction of type I and type II is given by one-electron perturbation theory (with neglect of overlap) [3] to

$$\delta E = \delta E_I + \delta E_{II}$$

$$\delta E_I = \frac{\langle \pi | H | p \rangle^2}{E_p - E_\pi}$$

$$\delta E_{II} = \frac{\langle \sigma | H | \pi^* \rangle^2}{E_\sigma - E_{\pi^*}}$$



The increase of energy is a sum of two hyperbolic functions, I as the electrophilic and II as the nucleophilic branch [3].

The following cases can be differentiated:

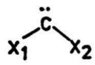
(a) $|\delta E_I| \gg |\delta E_{II}|$, *electrophilic carbene*

Raising the energy of the π-bonding level in olefines by introduction of electron donating substituents (*e.g.* methoxy groups, *etc.*) enhances the addition reaction. Its experimental verification has been well established [4].

(b) $|\delta E_I| \ll |\delta E_{II}|$, *nucleophilic carbene*

This requires (b1) the elevation of the σ-orbital and/or (b2) the empty p-AO (MO) of the carbene. Only the latter case (b2) has been verified in nucleophilic carbenes, such as cycloheptatrienylidene or cyclopropenylidene in which the *nonbonding* p-AO (of methylene) is replaced by an *antibonding* MO of the cyclic π-conjugated system.

The former case (b1), the lifting of the doubly occupied σ-orbital is met in carbenes of the type



where X_1 (X_2) are electron donating or accepting groups or atoms, and represent a *combination* of inductive and mesomeric effects.

According to the Walsh rules [5] the p-character of the σ-orbital (and hence its energy) raises with decreasing electronegativity of X_1, X_2 resp. In other words it will increase in the order of X_1 (X_2) = $F < OCH_3 < N(CH_3)_2$ *etc.*, and as supported by *ab initio* calculations (here not included). To our knowledge a systematic investigation of this effect

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on the nucleophilicity of carbenes (orbital energy of σ) has not been reported so far [6].

(c) $|\delta E_I| \sim |\delta E_{II}|$, *electrophilic + nucleophilic ("ambiphilic")* [7] *carbene*

Its reactivity is increased by introduction of electron donating or electron releasing substituents into the olefin.

The present approach towards carbene reactivity has a clear advantage over the characterization with Hammett parameters [7a]: (1) It accounts for the substrate dependence of the carbene reactivity. (2) The electrophilic and nucleophilic properties of singlet carbenes can be recast in terms of the Pauling electronegativity of X_1, X_2 resp., whereby (3) the orbitals required for the computations of δE_I and δE_{II} can be easily evaluated by simple Hueckel theory [3a]. A more detailed analysis of these considerations will be presented in a forthcoming report [8].

Note added to proof

While this manuscript has been submitted for publication a study has appeared (R. A. Moss, M. Fedorynski and W.-C. Shieh, J. Amer. Chem. Soc. **101**, 4736 (1979)) and which is in conformity with our conclusions.

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