

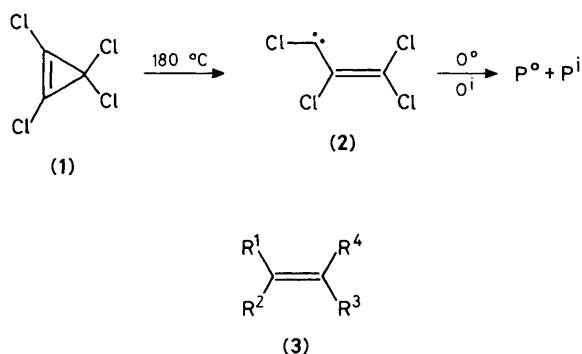
Perchlorovinylcarbene: a Bulky Electrophile

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The carbene selectivity index m_{CXY} for perchlorovinylcarbene $[\text{Cl}_2\text{C}=\text{CCl}(\text{Cl}):]$ was determined by competition experiments with different substituted olefins as ~ 0.38 , whereas the value calculated from Moss's equation is 0.34 ± 0.1 ; this proves at least qualitatively that perchlorovinylcarbene is an electrophilic carbene.

Upon thermal ring opening tetrachlorocyclopropene (1) apparently yields perchlorovinylcarbene (2) which efficiently adds to olefinic C=C bonds and inserts into aliphatic C-H bonds.^{1,2} Although the ground-state multiplicity of this interesting carbene is unknown, the stereochemical features of its cycloadducts¹ seem to indicate either a singlet ground state or a triplet with at most a small singlet-triplet energy gap.³ As an application of the utility of a recent kinetic classification scheme for carbenes⁴ we have now tested the relative reactivity of (2) towards various substituted olefins.



- a; $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{Me}$
 b; $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Me}, \text{R}^4 = \text{H}$
 c; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{Et}, \text{R}^3 = \text{R}^4 = \text{H}$
 d; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{R}^3 = \text{H}, \text{R}^4 = \text{Pr}^n$
 e; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{R}^4 = \text{H}, \text{R}^3 = \text{Pr}^n$
 f; $\text{R}^1 = \text{R}^3 = \text{Et}, \text{R}^2 = \text{R}^4 = \text{H}$
 g; $\text{R}^1 = \text{Pr}^n, \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$
 h; $\text{R}^1 = \text{Bu}^n, \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$
 i; $\text{R}^1 = \text{R}^2 = \text{Me}, \text{R}^3 = \text{CO}_2\text{Me}, \text{R}^4 = \text{H}$
 j; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{R}^4 = \text{H}, \text{R}^3 = \text{CO}_2\text{Et}$
 k; $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}, \text{R}^4 = \text{CO}_2\text{Et}$

Table 1. Competition constants $K = k_i/k_o$ for perchlorovinylcarbene (2) additions to various olefins at $180 \pm 2^\circ\text{C}$. Values for dichlorocarbene at -15°C were taken from ref. 5.

Olefin	(2)		:CCl ₂	
	k_i/k_o	$\log(k_i/k_o)$	k_i/k_o	$\log(k_i/k_o)$
(3a)	1.0	0	1.0	0
(3b)	1.44(19)	0.158	0.40 ^a	-0.40
(3c)	0.62(3)	-0.21	0.102	-0.99
(3d)	0.63(2)	-0.20	0.017 to 0.030 ^b	-1.50 to -1.76
(3e)	0.20(1)	-0.70	0.018 ^b	-1.74
(3f)	0.16(1)	-0.80	0.0134 ^a	-1.87
(3g)	0.14(2)	-0.85	0.0026	-2.59
(3h)	0.24(5)	-0.62	0.0035	-2.46
(3i)	0.12(3)	—	—	—
(3j)	0.19(2)	—	—	—
(3k)	0.35(5)	—	—	—

^a Value at 0°C . ^b Values for different 1,2-disubstituted olefins.

A series of typical competition experiments were carried out by studying the reaction of (1) at $180 \pm 2^\circ\text{C}$ with a large enough excess (≥ 10 fold) of two olefins. 2,3-Dimethylbut-2-ene (3a) was the standard olefin at 0°C , and product ratios P^1/P^0 were determined by vapour-phase chromatography using authentic reference samples.^{1,2}

The competition constants for various tri-, di-, and mono-substituted olefins (see Table 1) indicate that the cheletropic attack of perchlorovinylcarbene (2) must be more sensitive to steric hindrance than that of dichlorocarbene.⁶ Thus 2-methylbut-2-ene (3b) reacts faster than the dimethylbutene (3a), and ethyl crotonate (3j) is more reactive than methyl dimethylacrylate (3i). In addition, the direct competition between disubstituted olefins gave ratios of $k(3d)$ to $k(3e)$ of 3.2 ± 0.1 and $k(3d)$ to $k(3f)$ of 3.91 ± 0.09 , respectively, confirming the sensitivity to steric shielding. Consequently, the effect of temperature on the addition rates of perchlorovinylcarbene (2) would depend on the degree of substitution at the double bond, and a more pronounced dependence would be found than that for :CCl₂ additions.⁶ In spite of this obvious difficulty,⁷ values of $\log K = \log[k_i/k_o\{(2), +180^\circ\text{C}\}]$ were plotted against $\log K = \log[k_i/k_o\{:\text{CCl}_2, -15^\circ\text{C}\}]$ (see Figure 1). The slope of this expectedly poor correlation gave the carbene selectivity index⁴ m for (2) of ~ 0.38 .

$$m_{\text{CXY}} = -1.10 \sum_{\text{X,Y}} \sigma_{\text{R}^+} + 0.53 \sum_{\text{X,Y}} \sigma_{\text{I}} - 0.31 \quad (1)$$

From the dual-substituent parameter correlation (1) of Moss,⁴ m for (2) was calculated to be 0.34 ± 0.1 with $\sigma_{\text{R}^+}(\text{Cl}_2\text{C}=\text{CCl})$ estimated as 0.00 ± 0.1 and $\sigma_{\text{I}}(\text{Cl}_2\text{C}=\text{CCl}) \sim 0.36$.⁸ Although the uncertainties in these estimates mean

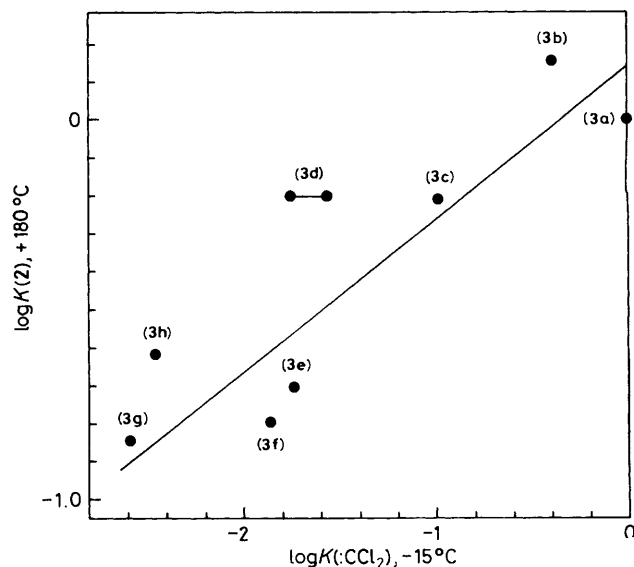


Figure 1. Correlation between relative reactivities of (2) at 180°C and :CCl₂ at -15°C with the alkenes (3a)–(3h) [$\log K = \log(k_i/k_o)$].

that any interpretation must be made with caution, the agreement between the observed and calculated m value for (2) is surprisingly good. At least qualitatively these values prove that perchlorovinylcarbene is an electrophilic carbene with a selectivity similar to that of ClCCO_2Et .⁴

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