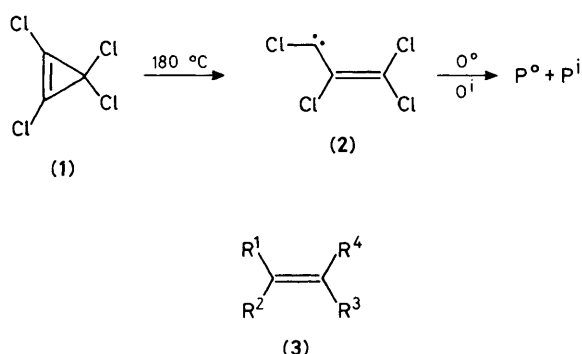# Perchlorovinylcarbene: a Bulky Electrophile

Rafael Kostikov* and Armin de Meijere*

Institute of Chemistry, University of Leningrad, Srednij pr. 41, 199004 Leningrad B-4, U.S.S.R., and Institut für Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, Federal Republic of Germany

The carbene selectivity index m_{CXY} for perchlorovinylcarbene [$Cl_2C=CClC(Cl)$:] 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 cycloadducts[1] 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 carbenes[4] we have now tested the relative reactivity of (2) towards various substituted olefins.

A series of typical competition experiments were carried out by studying the reaction of (1) at 180 ± 2 °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^i/P^o 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 $:CCl_2$ additions.[6] In spite of this obvious difficulty,[7] values of $\log K = \log[k_i/k_o\{(2), +180 °C\}]$ were plotted against $\log K = \log[k_i/k_o(:CCl_2, -15 °C)]$ (see Figure 1). The slope of this expectedly poor correlation gave the carbene selectivity index[4] m for (2) of ~0.38.

(1) → (2) → $P^o + P^i$

(3)

a; $R^1 = R^2 = R^3 = R^4 = Me$
b; $R^1 = R^2 = R^3 = Me, R^4 = H$
c; $R^1 = Me, R^2 = Et, R^3 = R^4 = H$
d; $R^1 = Me, R^2 = R^3 = H, R^4 = Pr^n$
e; $R^1 = Me, R^2 = R^4 = H, R^3 = Pr^n$
f; $R^1 = R^3 = Et, R^2 = R^4 = H$
g; $R^1 = Pr^n, R^2 = R^3 = R^4 = H$
h; $R^1 = Bu^n, R^2 = R^3 = R^4 = H$
i; $R^1 = R^2 = Me, R^3 = CO_2Me, R^4 = H$
j; $R^1 = Me, R^2 = R^4 = H, R^3 = CO_2Et$
k; $R^1 = R^2 = R^3 = H, R^4 = CO_2Et$

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

From the dual-substituent parameter correlation (1) of Moss,[4] m for (2) was calculated to be 0.34 ± 0.1 with $\sigma_{R^+}(Cl_2C=CCl)$ estimated as 0.00 ± 0.1 and $\sigma_I(Cl_2C=CCl)$ ~ 0.36.[8] Although the uncertainties in these estimates mean

Table 1. Competition constants $K = k_i/k_o$ for perchlorovinylcarbene (2) additions to various olefins at 180 ± 2 °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.
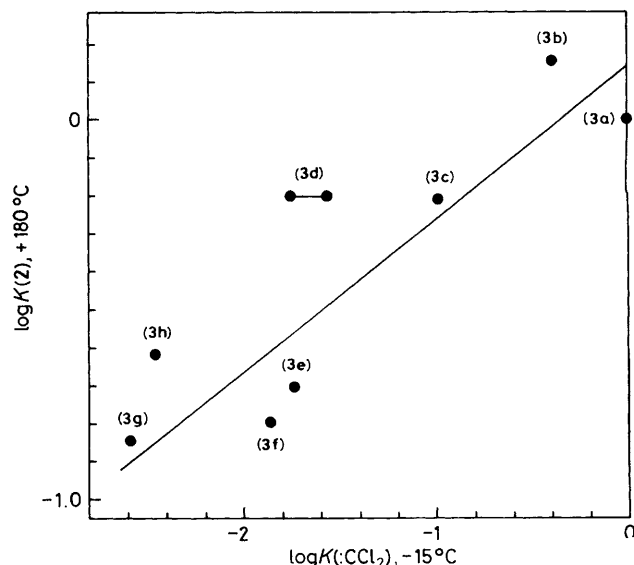

Figure 1. Correlation between relative reactivities of (2) at 180 °C and :CCl$_2$ at −15 °C with the alkenes (3a)—(3h) [$\log K = \log(k_i/k_o)$].

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]

Received, 5th July 1984; Com. 962

References

1 W. Weber and A. de Meijere, *Angew. Chem.*, 1980, **92**, 135; *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 138; W. Weber and A. de Meijere, *Chem. Ber.*, 1984, **117**, in the press.

2 Th. Liese, G. Splettstoesser, and A. de Meijere, *Tetrahedron Lett.*, 1982, **23**, 3341.

3 *Cf.* R. A. Moss and M. A. Jones, Jr., in 'Reactive Intermediates,' Vol. 2, eds. M. A. Jones, Jr., and R. A. Moss, Wiley–Interscience, New York, 1981, pp. 59ff., and refs. cited therein.

4 R. A. Moss, *Acc. Chem. Res.*, 1980, **13**, 58, and refs. cited therein. See also W. W. Schoeller, *Tetrahedron Lett.*, 1980, **21**, 1505, 1509.

5 W. von E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, 1958, **80**, 5274; D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and M. E. Burlitch, *ibid.*, 1967, **89**, 959.

6 B. Giese and C. Neumann, *Tetrahedron Lett.*, 1982, **23**, 3557.

7 B. Giese, Woo Bung Lee, and C. Stiehl, *Tetrahedron Lett.*, 1983, **24**, 881.

8 'Correlation Analysis in Chemistry,' eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1978, p. 507. σ_R+ was estimated on the following basis: $\sigma_R+ \sim \sigma_R° - 0{\cdot}15$; $\sigma_R°(F) \sim \sigma_R°(Cl)$; $\sigma_R°(C_2F_3) \sim 0.14$.