

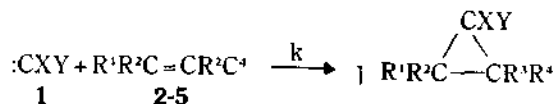
## Selectivity of Dihalocarbenes in Cycloaddition Reactions

Woo Bung Lee, Jeong Ho Lee, and Si Ho Kim

Department of Chemistry, Kyungpook National University, Taegu 635

Received January 28, 1986

In cycloaddition reactions of methylsubstituted alkenes **2**, the selectivities of singlet carbenes **1** depend on inductive and resonance effects of substituents X and Y'. The absence of



**2:** R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> = CH<sub>3</sub>, H

**3:** R<sup>1</sup> = alkyl, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H

**4:** R<sup>1</sup> = alkyl, R<sup>2</sup> = CH<sub>3</sub>, R<sup>3</sup> = R<sup>4</sup> = H

**5:** R<sup>1</sup> = alkyl, R<sup>2</sup> = H, R<sup>3</sup> = R<sup>4</sup> = CH<sub>3</sub>

Table 1. Relative Rates  $k_{\text{CCl}_2}$  and  $k_{\text{CBr}_2}$  of Carbenes CCl<sub>2</sub> and CBr<sub>2</sub> in Cycloadditions with Alkenes 3-5 at 25°C

Substituent of the alkenes R	$k_{\text{CCl}_2}$ Cycloadditions with alkenes			$k_{\text{CBr}_2}$ Cycloadditions with alkenes	
	3 <sup>2</sup>	4 <sup>1</sup>	5	3 <sup>2</sup>	4 <sup>1</sup> 5
a:CH <sub>3</sub>	12	320	1000	500	1000
b:C <sub>2</sub> H <sub>5</sub>	9.1	210		68	480
c:i-C <sub>3</sub> H <sub>7</sub>	4.4	77	280	30	160 350
d:CH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		29		60	
e:C(CH <sub>3</sub> ) <sub>3</sub>	0.47	14	110	2.5	38 185

steric parameters indicates that the steric repulsion between methyl groups of the alkenes and substituents X and Y of the carbenes is negligible. Nevertheless, rate retarding effects have been observed in the cycloaddition reactions of alkenes 3<sup>2</sup> and 4<sup>1</sup> which contain bulkier alkyl groups. A general linear free energy relationship, therefore, may involve steric interaction. To answer the question whether a common correlation for the reactions of singlet carbenes exists, we have measured relative rates of CCl<sub>2</sub> and CBr<sub>2</sub> cycloadditions with the alkenes 3-5 using the competition technique<sup>4</sup> (Table 1).

Plotting  $\log k_{\text{CBr}_2}$  vs  $\log k_{\text{CCl}_2}$  shows that the reactivities of CBr<sub>2</sub> and CCl<sub>2</sub> cannot be correlated with each other (Refer to Table 1). Instead of a straight line, each of the alkenes 3-5 gives a linear free energy relationship by itself (Figure 1). The slopes vary from 1.1 via 0.86 to 0.73 for the reactions of monoalkylated alkenes 3 via dialkylated alkenes 4 to trialkylated alkenes 5. This is in accord with the reactivity-selectivity principle<sup>5</sup> because the decrease in the selectivity ( $\log k_{\text{CBr}_2}/k_{\text{CCl}_2}$ ) parallels the increase in the reactivity ( $\log k_{\text{CBr}_2}$  and  $\log k_{\text{CCl}_2}$ ) of the alkenes.

With the methylsubstituted alkenes, the Skell-Moss line gives the proportionality factor of 0.65<sup>1</sup>. It is, thus, obvious that no common linear correlation exists between the reactivities of CBr<sub>2</sub> and CCl<sub>2</sub> if the number and the bulkiness of the alkyl groups at the alkenes are different. This may not however necessarily exclude a general relationship between selectivities ( $k_{\text{CXY}}/k_{\text{CCl}_2}$ ) and substituent parameters of carbenes and alkenes. Such a correlation should follow the

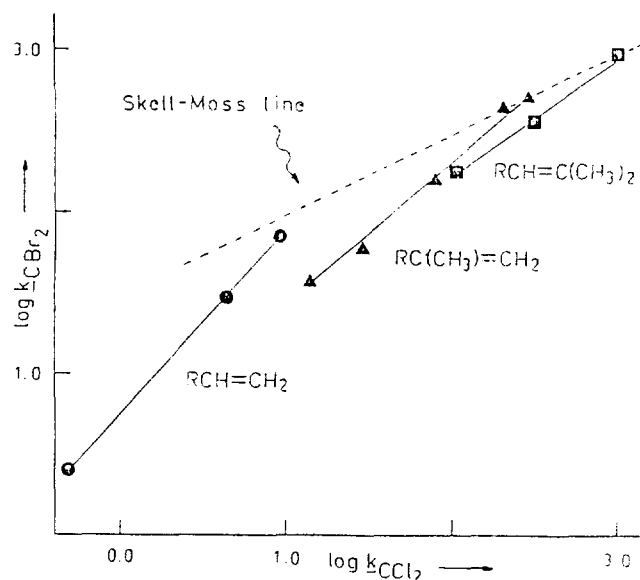


Figure 1. Correlations between the relative reactivities of CBr<sub>2</sub> and CCl<sub>2</sub> in cycloadditions with alkenes 3-5.

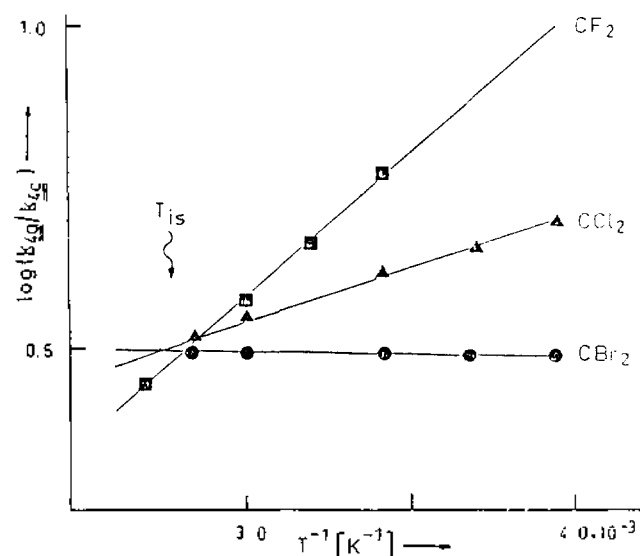


Figure 2. Temperature effect on the selectivity of carbenes in the competition system 4a/4c.

condition of a constant isoselective temperature  $T_{is}$ <sup>5</sup> which is  $90 \pm 10^\circ\text{C}$  for the Skell-Moss equation.<sup>6</sup> When  $T_{is}$  remains in the range of  $90 \pm 10^\circ\text{C}$ , substituent's steric effect could be incorporated into the relationship. We have carried out experiments with alkene 4c (R = i-C<sub>3</sub>H<sub>7</sub>) which deviates from the Skell-Moss relationship. Measurements in the competition system 4a/4c between  $-20$  and  $100^\circ\text{C}$  show that the selectivity lines of CF<sub>2</sub><sup>7</sup>, CCl<sub>2</sub> and CBr<sub>2</sub> cross also between 80 and

100°C (Figure 2). When increasing temperature the selectivity of  $\text{CF}_2$  decrease, and that of  $\text{CBr}_2$  increase, with the result that at approximately 90°C all the dihalocarbenes show the *identical* selectivity indicating isoselective temperature is approximately 90°C. Above this temperature, inverse selectivity is obeyed *i.e.*  $\text{CF}_2$  becomes less selective and  $\text{CBr}_2$  more selective.\* The constant isoselective temperature may satisfy the requirement that the polar and the steric effect are to be equally well correlated with the selectivities  $\log(k_{\text{CBr}_2}/k_{\text{CF}_2})$ . Further work is in progress.

**Acknowledgement.** This research was supported by a grant from the Korea Science and Engineering Foundation (KOSEF).

#### References and Notes

1. R.A. Moss, *Acc. Chem. Res.*, **13**, 58 (1980).
2. R.A. Moss, M.A. Joyce and J.K. Huselton, *Tetrahedron Lett.*, 4621 (1975).
3. B. Giese and C. Neumann, *Tetrahedron Lett.*, 3557 (1982).
4. B. Giese, W.B. Lee and J. Meister, *Liebigs Ann. Chem.*, 725 (1980).
5. B. Giese, *Angew. Chem.*, **89**, 162 (1977); *Angew. Chem. Int. Ed. Engl.*, **16**, 125 (1977).
6. B. Giese, W.B. Lee, *Angew. Chem.*, **92**, 864 (1980); *Angew. Chem. Int. Ed. Engl.*, **19**, 835 (1980).
7. The carbenes  $\text{CF}_2$  were generated using the method of D.J. Burton and D.G. Nase, *J. Am. Chem. Soc.*, **95**, 8467 (1973). Detailed procedure: C.W. Jefford, J. Mareda, J.C.E. Gehret, T. Kabengele, W.D. Graham and U. Burger, *J. Am. Chem. Soc.*, **89**, 2585 (1976).
8. C. Wentrup, "Reactive Molecules", Wiley-Interscience, New York, 1984.