Tetrahedron Vol. 41, No. 8, pp. 1565 to 1566, 1985
Printed in Great Britain.

0040-4020/85 \$3.00 + .00
Pergamon Press Ltd.

DEVIATING BEHAVIOUR OF BROMOCARBETHOXYCARBENE IN CYCLOADDITION REACTIONS

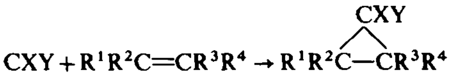
B. GIESE,* W. H. MEHL and W. B. LEE

Institut für Organische Chemie und Biochemie der Technischen Hochschule, Petersenstr. 22,
D-1600 Darmstadt, West Germany

(*Received in USA* 5 *December* 1983)

Abstract—The effect of Me substituents at alkenes **4** on the rates and activation parameters of cycloaddition reactions of bromocarbethoxycarbene (**3**) is very small. This carbene does not fit into the general equation (b) and the isoselective relationship (c) of dihalocarbenes. The deviating behaviour can be explained by a diffusion controlled reaction rate of bromocarbethoxycarbene.

Recently we have shown that selectivities of dihalocarbenes CXY in cycloaddition reactions with methylsubstituted alkenes coincide at 90 ± 10°.[1] At this isoselective temperature (T_{is}) the selectivities m_{CXY} which are described at 25° by the Moss equation (a)[2] are 1.0.[3] Therefore, only those carbenes fit into the general linear free energy relationship (b)[3] with temperature dependent parameters a, b and c that follow the same isoselective relationship (c)[4] with $T_{is} = 90 \pm 10°$.



$$CXY + R^1R^2C{=}CR^3R^4 \rightarrow R^1R^2C(CXY)CR^3R^4$$

$$25°: m_{CXY} = -1.10 \sum_{XY} \sigma_R^+ + 0.53 \sum_{XY} \sigma_I - 0.31 \quad (a)$$

$$m_{CXY} = a_{XY}\sigma_R^+ + b_{XY}\sigma_I + c \quad (b)$$

$$\delta_{CXY}(\Delta H_m^{\ddagger} - \Delta H_n^{\ddagger}) = T_{is} \cdot \delta_{CXY}(\Delta S_m^{\ddagger} - \Delta S_n^{\ddagger}) \quad (c)$$

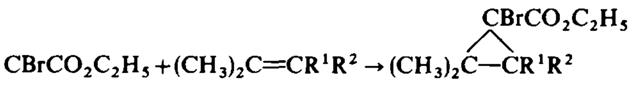
Selectivities of carbenes with small m_{CXY}-values at 25° should, therefore, exhibit a large temperature dependence in order to cross the selectivities of dihalocarbenes at 90°. At 25° m_{CXY} of the carbene $CBrCO_2C_2H_5$ (**3**) has been reported to be 0.29.[5] To prove whether this carbene belongs to relationships (b) and (c) we have measured the competition coefficients with alkenes **4a–c** at different temperatures (Table 1). The carbenes were generated by photolysis of ethyl bromodiazoacetate **2** which has been prepared from diazoacetic ester **1** according to literature procedure.[6]

The data of Table 1 show that the temperature effect on the selectivity of $CBrCO_2C_2H_5$ (**3**) is so small, that it does not belong to the isoselective relationship (c) of the dihalocarbenes. This becomes obvious by plotting the selectivities of the carbenes in an Eyring diagram (Fig. 1). Whereas all dihalocarbenes cross each other at 90° the selectivity of $CBrCO_2C_2H_5$ deviates dramatically from this point of intersection. Therefore, relationships (b) and (c) do not hold for $CBrCO_2C_2H_5$ (**3**) and the fit with the Moss equation (a)[5] is only fortuitous.

An explanation for the different behaviour of $CBrCO_2C_2H_5$ can be deduced from the data of Table 1. They demonstrate that the Me groups at the alkenes **4** have nearly no effect on the rates and the activation enthalpies (no temp effect) of the cycloaddition reactions of carbene **3**. This absence of substituent effects is typical for diffusion controlled reactions. Some arylchlorocarbenes **6** approach the value for diffusion controlled reactions in cycloadditions with dimethylbutene **4c**.[7] Because bromine stabilizes singlet carbenes less than chlorine and the ester group is a powerful electron-withdrawing substituent, carbene **3** should be even more reactive than **6**.

Relationships (a) and (b) that describe the substituent influence on the selectivity cannot hold for

$$\underset{\mathbf{1}}{N_2CHCO_2C_2H_5} \xrightarrow[(2)\ BrCN]{(1)\ Ag_2O} \underset{\mathbf{2}}{N_2CBrCO_2C_2H_5} \xrightarrow[-N_2]{h\nu} \underset{\mathbf{3}}{CBrCO_2C_2H_5}$$



$$CBrCO_2C_2H_5 + (CH_3)_2C{=}CR^1R^2 \rightarrow (CH_3)_2C(CBrCO_2C_2H_5)CR^1R^2$$

3 **4** **5**

4,5	R^1	R^2
a	H	H
b	CH_3	H
c	CH_3	CH_3

CClAr
6

$CClCF_3$
7

carbenes that react with a diffusion controlled rate. The breakdown of relationship (b), the very small substituent effect on the rate and the absence of a temperature influence makes it very likely that $CBrCO_2C_2H_5$ (3) reacts with a diffusion controlled rate at least with **4b** and **4c**. A similar behaviour should be observed with (trifluoromethyl)-chlorocarbene (7) which reacts also with a very low selectivity at 30° ($m_{CClCF_3} = 0.19$).[8] As has been pointed out by Moss *et al.*[8] a diffusion controlled rate could explain the deviation of the observed m_{CXY}-value of 7 from the calculated one.

Table 1. Competition coefficients $k_{4b}:k_{4a}$ and $k_{4c}:k_{4b}$ of $CBrCO_2C_2H_5$ (3) in cycloaddition reactions with alkenes **4a–c** (mean error ± 10%)

Temperature (°C)	$k_{4b}:k_{4a}$	$k_{4c}:k_{4b}$
−50	1.77	1.21
−20	1.83	1.13
0	1.80	1.06
25	1.79	1.04

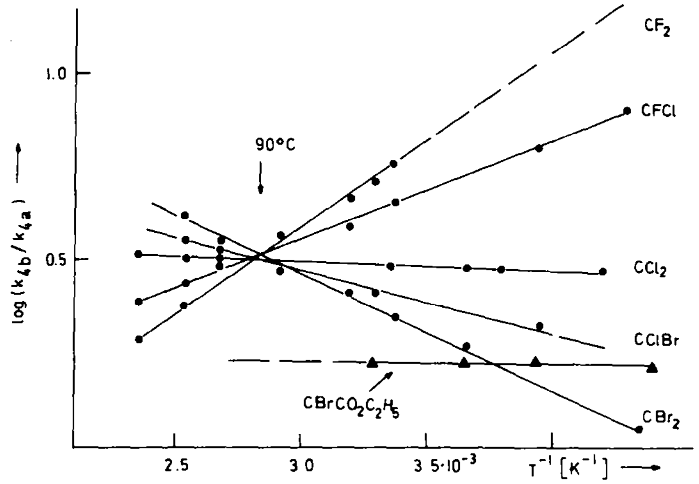


Fig. 1. Temperature influence on the selectivity of dihalocarbenes and bromocarbethoxycarbene (3) in a methyl-2-butene (**4b**)/isobutene (**4a**)-competition system.

EXPERIMENTAL

Ethyl bromodiazoacetate 2 is synthesized according to literature procedure from ethyl diazoacetate 1.[6] Photolysis of 2 in the presence of alkenes **4a–c** gives products **5a–c**.[6]

Competition experiments. About 0.5 mol of ethyl bromodiazoacetate 2 was dissolved in 30 mmol of methylbutene **4b** or dimethylbutene **4c** and mixed with 15–35 mmol of isobutene **4a**. The sealed glass tubes were irradiated for 14 hr by a 125 W mercury lamp. After distillation of alkenes the ratios of the concentrations of cyclopropanes **5a–c** are measured by gas chromatography. According to pseudo-first order kinetics[4] the competition constants of Table 1 are calculated.

Acknowledgement—This work was supported by the Fonds der Chemischen Industrie.

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