

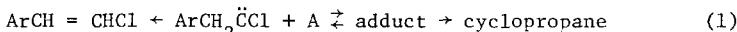
ADDITION OF AN ELECTROPHILIC CARBENE TO AN ELECTRON-DEFICIENT OLEFIN.
KINETICS OF BENZYLCHLOROCARBENE-DIETHYL FUMARATE REACTION

Michael T. H. Liu* and R. Subramanian

Department of Chemistry, University of Prince Edward Island
Charlottetown, Prince Edward Island, Canada C1A 4P3

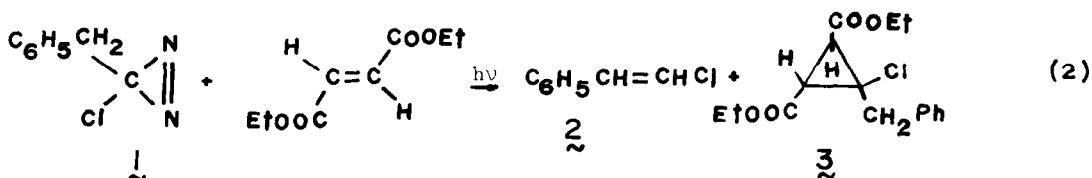
Summary: Benzylchlorocarbene reacts as an electrophile with electronic deficient diethyl fumarate; the dependence of product ratio on [DEF] is consistent with formation of a carbene adduct.

Carbene addition to nucleophilic olefins has been the subject of intensive investigations.¹ Turro and Moss have measured the absolute rate constants for the chlorophenylcarbene addition to electron rich alkenes such as tetramethylethylene (TME) by laser photolysis.² The results were interpreted in terms of a kinetic model in which a dissociable carbene-alkene adduct is reversibly formed. Similar involvement of carbene-alkene intermediate was also proposed by Tomioka and Liu³ in the photolysis of 3-chloro-3-benzyldiazirine in the presence of alkenes, eq. (1).



Warner⁴ has suggested that the results of this investigation³ could be accommodated by a mechanism in which chlorostyrene arises from the free carbene and its excited state. In contrast to the studies on electron-rich alkenes, the reaction of phenylchlorocarbene with α,β -unsaturated esters and nitriles has been studied by Doyle and coworkers.⁵ We have investigated the kinetics of benzylchlorocarbene addition to diethyl fumarate (DEF) and our findings on the philicity of this carbene towards the electron-deficient olefin as well as the kinetic order with respect to the substrate are reported here.

3-Chloro-3-benzyldiazirine (1) was synthesized from benzylamidine hydrochloride by Graham's method.⁶ Photolysis of 1 (0.01M) in the presence of excess DEF (0.1-0.6M) in isoctane using a 250W GE sunlamp (CS-052 filter, cut off at 350nm) afforded a simple mixture⁷ of E and Z β -chlorostyrenes (2) and the cyclopropane 3 according to eq. (2).



Product ratios, $3/2$ and $2Z/2E$, for various temperatures and concentrations of DEF are reported⁷ in Table 1.

Table 1: Product Distribution in the Photolysis of 1 and Diethylfumarate in Isooctane.

T, °C [DEF] M	8.5		15.1		25.2		36.3		45.2	
	2Z/2E	3/2	2Z/2E	3/2	2Z/2E	3/2	2Z/2E	3/2	2Z/2E	3/2
0.10	0.22	0.205	0.22	0.162	0.22	0.109	0.22	0.078	0.22	0.064
0.15	0.23	0.277	0.23	0.220	0.23	0.152	0.23	0.105	0.23	0.086
0.20	0.24	0.319	0.24	0.265	0.23	0.192	0.24	0.132	0.23	0.103
0.30	0.26	0.401	0.25	0.327	0.24	0.233	0.24	0.166	0.24	0.130
0.40	0.26	0.440	0.25	0.389	0.25	0.262	0.25	0.192	0.25	0.155
0.60	0.27	0.506	0.28	0.396	0.26	0.315	0.25	0.234	0.25	0.184
k_i/k_t	0.346 ±0.007		0.452 ±0.019		0.712 ±0.025		1.01 ±0.014		1.23 ±0.015	

The dependence of $\beta/2$ on [DEF] exhibits pronounced curvature (Fig. 1). This behaviour can be attributed to the existence of an intermediate in the reaction pathway.

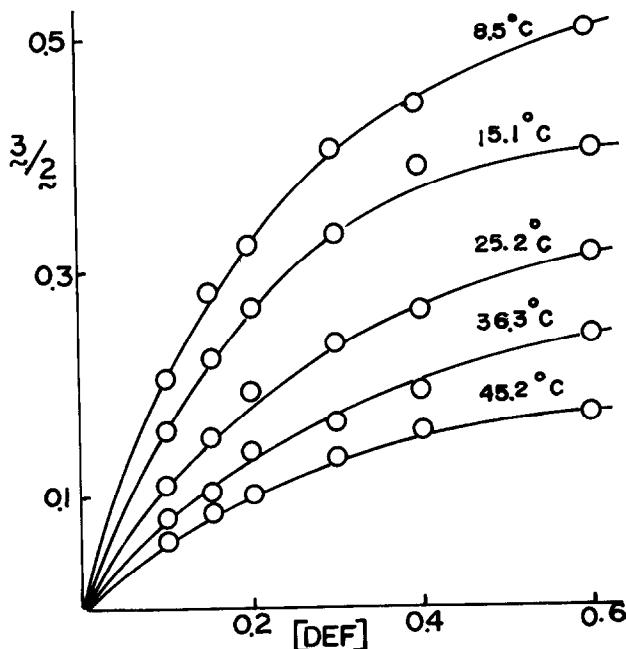


Fig. 1 Plots of 3/2 vs [DEF]

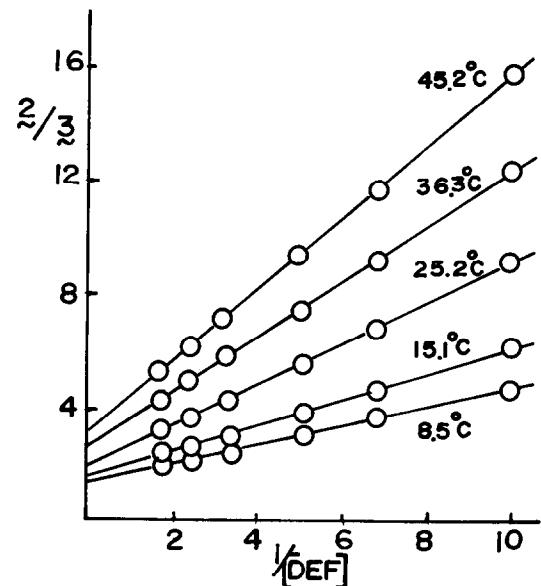
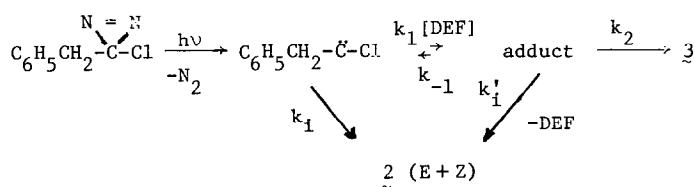


Fig. 2 Plots of $2/3$ vs $1/[DEF]$

Scheme 1



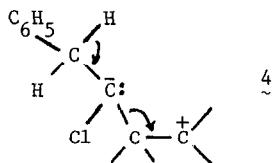
Scheme 1 is proposed to account for the kinetic results. The carbene⁸ gives rise, by two competing reactions, to the chlorostyrene by an intramolecular 1,2-H shift or react with DEF yielding a reversibly-formed adduct. The adduct can collapse to the cyclopropane or decompose to $\underline{2}$ with the elimination of DEF.

Application of steady state treatment to Scheme 1 gives eq. 3.

$$\frac{2}{3} = \frac{k_i'}{k_2} + \frac{k_i}{k_t} \cdot \frac{1}{[DEF]} \quad (3)$$

where the overall rate constant for cyclopropanation, k_t , is equal to $k_1 k_2 / (k_{-1} + k_2 + k_i')$. This expression predicts a linear relationship between $\frac{2}{3}$ and the reciprocal of [DEF]. Plots of $\frac{2}{3}$ vs $\frac{1}{[DEF]}$ are linear (Fig. 2) with correlation coefficient > 0.99 . The values of k_i/k_t were derived from the slopes in fig. 2 and from their temperature dependency, the quantities $E_i - E_t = 6.3 \pm 0.3 \text{ kcal/mol}$ and $A_i/A_t = 10^{4.4 \pm 0.2}$ were evaluated. If the rate constant for the 1,2-H shift⁹ is taken to be $k_i = 10^{12.2} \exp^{-\frac{6400}{RT}} \text{ s}^{-1}$, then E_t and A_t are 0.1 kcal/mol and $10^{7.8} \text{ M}^{-1} \text{ s}^{-1}$ respectively. The fact that $E_t \approx 0$ provides good evidence that the reaction of the carbene with DEF is not a one step process.²

In the photolysis of $\underline{1}$ in TME the Z/E ratio of $\underline{2}$ was found to increase from 0.30 to 0.67 as the [TME] increases from 0.1 to 1.4 M.⁹ This could be explained on the basis that the carbene conformer leading to E isomer is more reactive to external alkene than the Z conformer due to steric hindrance in the latter.¹⁰ Therefore the E conformer is preferentially trapped by TME to give an adduct (4) which can undergo 1,4-anti-elimination to chlorostyrene.



In the present reaction the change in $\underline{2}Z/\underline{2}E$ ratio is relatively small (0.22-0.27 when $[\text{DEF}] = 0.1-2.0 \text{ M}$) because the adduct here is destabilized by the ester groups making the trapping of the E conformer of the carbene unfavourable.

If the mechanism involving excited state carbene were operative, the $\underline{2}Z/\underline{2}E$ ratios should be independent of the nature of the substrate. However, the observation of substrate dependent stereochemistry seems to support the intermediacy of an adduct rather than an excited carbene.

In the thermolysis of phenylchlorodiazirine with electron-poor alkenes, Doyle and co-workers⁵ proposed a mechanism involving the initial interaction of the carbene with the olefin to give a nucleophilic ylide which subsequently reacts with another molecule of olefin to produce the cyclopropane. With respect to the cyclopropanation of benzylchlorocarbene with DEF, only one isomer of $\underline{3}$ was obtained. The observation that the reaction is first order in DEF suggests that the nucleophilic ylide-olefin reaction may not be slow. The lower reactivity of DEF ($k_t/k_i = 1.40$ at 25°C) as compared with that of TME ($k_t/k_i = 10.4$ at 24°C) indicates that the carbene acts as an electrophile. This can be further substantiated by the results of the laser studies on the reaction of substituted chlorophenyl-

carbenes with DEF. The absolute rate constants¹¹ for $p\text{-NO}_2\text{C}_6\text{H}_4\text{-}\ddot{\text{C}}\text{-Cl}$, $\text{C}_6\text{H}_5\text{-}\ddot{\text{C}}\text{-Cl}$ and $p\text{-CH}_3\text{OC}_6\text{H}_4\text{-}\ddot{\text{C}}\text{-Cl}$ with DEF are 1.0×10^8 , 3.8×10^6 and $6.3 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ respectively which is in agreement with an electrophilic carbene addition. It may be noted that $E_i - E_t = 8.1 \pm 0.2 \text{ kcal/mol}$ for the reaction of I with TME⁹ and therefore $E_t(\text{DEF}) > E_t(\text{TME})$ by 1.8 kcal/mol which also is in accord with the interpretation that benzylchlorocarbene behaves as an electrophilic species.

Photolysis of I in diethyl maleate was found to yield only trace amounts of cyclopropane and therefore the possible involvement of a nucleophilic ylide, as proposed by Doyle and coworkers, could not be tested.

Acknowledgement: We thank the Natural Sciences and Engineering Research Council of Canada and the University of Prince Edward Island for financial support.

References and Notes

- (1) R. A. Moss, in 'Carbenes,' vol. 1, M. Jones, Jr. and R. A. Moss, eds. Wiley, New York, 1973, pp. 153-304; R. A. Moss and M. Jones, Jr. in 'Reactive Intermediates,' M. Jones, Jr. and R. A. Moss, eds., Wiley, New York, vol. 1, 1978, pp. 69-116; vol. 2, 1981, pp. 59-134; R. A. Moss, Acc. Chem. Res., 13, 58 (1980).
- (2) N. J. Turro, G. F. Lehr, J. A. Butcher, R. A. Moss, and W. Guo, J. Am. Chem. Soc., 104, 1754 (1982). R. A. Moss, L. A. Perez, N. J. Turro, I. R. Gould, and N. P. Hacker, Tetrahedron Lett., 24, 685 (1983).
- (3) H. Tomioka, N. Hayashi, Y. Izawa, and M. T. H. Liu, J. Am. Chem. Soc., 106, 454 (1984).
- (4) P. M. Warner, Tetrahedron Lett., 25, 4211 (1984).
- (5) M. P. Doyle, J. W. Terpstra, and C. H. Winter, Tetrahedron Lett., 25, 901 (1984).
- (6) W. H. Graham, J. Am. Chem. Soc., 87, 4396 (1965).
- (7) Products were separated by column chromatography using silica gel and eluting with 95:5 pentane-diethyl ether. nmr: δ , δ (ppm), 1.25 (t,6H), 2.81 (m,2H), 3.30 (s,2H), 4.20 (q, 4H), 7.26 (s,5H); δ , δ (ppm), 7.38 (phenyl), AB quartet with the outer pairs centered at δ 6.63 and 6.78 (E-olefin-H) and AB quartet with the outer pairs centered at δ 6.08 and 6.63 (Z-olefinic-H). Relative yields of products were obtained by gas chromatographic analysis on a varian VISTA 6000 instrument using a 6ft. x 2mm(i.d) glass column packed with CSP-20M. Peak areas were integrated by a HP 3390A recorder.
- (8) The possibility of the reaction occurring through a diazo intermediate is unlikely since chlorodiazomethane was found to be stable only at 35°K. R. S. Sheridan and M. T. H. Liu. To be published.
- (9) M. T. H. Liu, J. Chem. Soc., Chem. Comm., in press (1985).
- (10) H. Tomioka, N. Hayashi, Y. Izawa, and M. T. H. Liu, J. Chem. Soc., Chem. Comm., 476 (1984).
- (11) D. Griller, M. T. H. Liu, and J. C. Scaiano. Unpublished results.

(Received in USA 29 March 1985)