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Substituent and Temperature Effects on the Reactions of Benzylchlorocarbene with Alcohol

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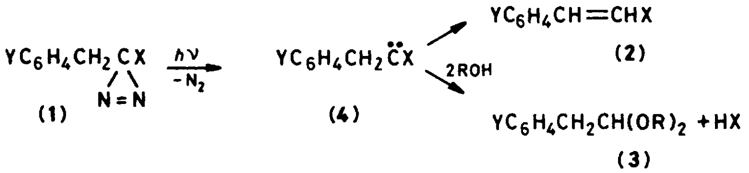
The insertion reaction of the *para*-substituted benzylchlorocarbenes with methanol shows a second-order dependence in methanol, but only a first-order dependence in ethylene glycol. The results are consistent with a mechanism whereby the carbene inserts into the O–H bond of the alcohol dimer or oligomer by electrophilic attack of the carbene on the oxygen lone pair to produce a reversibly formed ylide intermediate. The effects of the substituents indicate that electron-releasing group favours rearrangement while electron-withdrawing group facilitates insertion. Photolysis of halogenodiazirines in methanol at low temperatures give rise to V-shaped Arrhenius behaviour and the importance of N_2 in influencing the reactivity of the singlet halogenocarbene in the matrix is demonstrated.

Extensive investigations have been carried out on the interaction of carbene- and oxygen-containing compounds.[1] Recently, there is a revival of interest in the reaction of carbenes and alcohols.[2–7] Kirmse has suggested that the electrophilic or nucleophilic character of the carbene plays an important role in the mechanism of the O–H insertion reaction.[4] Also, it has been demonstrated that chlorocarbenes can show a strong discrimination in their reactivities towards methanol monomers and oligomers.[2] The kinetic behaviour for the reaction of singlet benzylchlorocarbene with methanol shows a second-order dependence in methanol.[5] To gain an understanding of the philicity of the chlorocarbene and the nature of the insertion reaction it is necessary to investigate the effect of substituents on the carbene–alcohol reaction. To this end, methodology previously developed by Liu and Subramanian[5] has been applied to study the kinetics of reaction of substituted benzylchlorocarbene with alcohol and the results are reported here.

Results and Discussion

3-Halogeno-3-benzyldiazirines were synthesized by Graham's method.[8] Photolysis of these diazirines (0.01M) in the presence of excess of alcohol in benzene gave *E*- and *Z*-β-halogenostyrenes (2), phenylacetaldehyde dialkyl acetals (3), and hydrogen halide by two competing reactions as shown in equation (1).



$$YC_6H_4CH_2\overset{N=N}{C}X \xrightarrow[-N_2]{h\nu} YC_6H_4CH_2\ddot{C}X \begin{cases} \rightarrow YC_6H_4CH{=}CHX & (2) \\ \xrightarrow{2ROH} YC_6H_4CH_2CH(OR)_2 + HX & (3) \end{cases} \quad (1)$$

(1a), (2a), (4a)	X = Cl,	Y = H	(3a) = (3d),	Y = H,	R = CH_3
(1b), (2b), (4b)	X = Cl,	Y = CH_3	(3b)	Y = CH_3	R = CH_3
(1c), (2c), (4c)	X = Cl,	Y = Cl	(3c)	Y = Cl,	R = CH_3
(1d), (2d), (4d)	X = Br,	Y = H	(3e)	Y = H,	R = C_2H_5
			(3f)	Y = Cl,	R = CH_2

The HCl (or HBr) so produced will react with the singlet benzylhalogenocarbene (4) in a secondary reaction to form 1-phenyl-2,2-dichloroethane (or 1-phenyl-2,2-dibromoethane). Since the dihalide amounts to only a few percent of the total product, its presence will not alter the kinetic argument which we present later.

The acetal:styrene product ratios were determined as a function of [ROH] and temperature for the reaction of methanol with 3-chloro-3-benzyldiazirine (1a),[5] 3-chloro-3-*p*-methylbenzyldiazirine (1b), 3-chloro-3-chlorobenzyldiazirine (1c), 3-bromo-3-benzyldiazirine (1d), and for the reactions of ethanol–(1a) and ethylene glycol–(1c). The data are presented in Tables 1—5.

In general, plots of acetal:styrene product ratios *versus* [ROH] exhibit pronounced curvature and the extrapolation to low alcohol concentration does not appear to go through the origin, indicating the existence of a limiting alcohol concentration below which insertion does not take place. Representative plots (Figure 1) are given for the reaction of diazirine (1b) with methanol. To conform this behaviour, the ratios (3a):(2a) were determined for the reaction of (1a) and methanol, with [MeOH] ranging from 0.02M to 0.1M (Figure 2). No acetal could be detected when [MeOH] was <0.03M; however, the production of chlorostyrene was still measurable.

Thus, it would appear that the curve does not go through the origin. This observation is consistent with the expectation that the reaction does indeed involve only dimer or other oligomers; such behaviour is not evident for the reaction of benzylchlorocarbene with alkene.[9] Since the hydrogen-bonded methanol oligomers are more reactive to chlorocarbenes than methanol monomer,[2] the O–H insertion process is unable to compete with the intramolecular 1,2-H shift at very low methanol concentrations. Hence chlorostyrene is produced exclusively.

Table 1. Product distribution in the photolysis of diazirine (**1b**) and MeOH in benzene

T/°C	8.5		14.1		19.5		24.5		29.5	
[MeOH]/M	$\frac{(\mathbf{3b})}{(\mathbf{2b})}$	$\frac{Z\text{-}(\mathbf{2b})}{E\text{-}(\mathbf{2b})}$	$\frac{(\mathbf{3b})}{(\mathbf{2b})}$	$\frac{Z\text{-}(\mathbf{2b})}{E\text{-}(\mathbf{2b})}$	$\frac{(\mathbf{3b})}{(\mathbf{2b})}$	$\frac{Z\text{-}(\mathbf{2b})}{E\text{-}(\mathbf{2b})}$	$\frac{(\mathbf{3b})}{(\mathbf{2b})}$	$\frac{Z\text{-}(\mathbf{2b})}{E\text{-}(\mathbf{2b})}$	$\frac{(\mathbf{3b})}{(\mathbf{2b})}$	$\frac{Z\text{-}(\mathbf{2b})}{E\text{-}(\mathbf{2b})}$
0.1	0.152	0.16	0.112	0.17	0.0819	0.16	0.0639	0.15	0.0551	0.17
0.15	0.316	0.18	0.229	0.17	0.198	0.18	0.152	0.17	0.116	0.19
0.20	0.499	0.20	0.406	0.19	0.308	0.19	0.243	0.19	0.197	0.19
0.30	0.736	0.22	0.645	0.22	0.537	0.22	0.453	0.21	0.441	0.22
0.40	0.987	0.25	0.862	0.24	0.735	0.24	0.626	0.23	0.552	0.23
0.60	1.21	0.28	1.14	0.28	0.08	0.27	0.960	0.28	0.879	0.28
1.0	1.55	0.33	1.48	0.32	1.38	0.32	1.30	0.32	1.21	0.31
2.0	1.89	0.37	1.64	0.36	1.55	0.36	1.50	0.36	1.48	0.34

Table 2. Product distribution in the photolysis of diazirine (**1c**) and MeOH in benzene

T/°C	0.6		8.9		15.1		20.1		25.0		30.0	
[MeOH]/M	$\frac{(\mathbf{3c})}{(\mathbf{2c})}$	$\frac{Z\text{-}(\mathbf{2c})}{E\text{-}(\mathbf{2c})}$	$\frac{(\mathbf{3c})}{(\mathbf{2c})}$	$\frac{Z\text{-}(\mathbf{2c})}{E\text{-}(\mathbf{2c})}$	$\frac{(\mathbf{3c})}{(\mathbf{2c})}$	$\frac{Z\text{-}(\mathbf{2c})}{E\text{-}(\mathbf{2c})}$	$\frac{(\mathbf{3c})}{(\mathbf{2c})}$	$\frac{Z\text{-}(\mathbf{2c})}{E\text{-}(\mathbf{2c})}$	$\frac{(\mathbf{3c})}{(\mathbf{2c})}$	$\frac{Z\text{-}(\mathbf{2c})}{E\text{-}(\mathbf{2c})}$	$\frac{(\mathbf{3c})}{(\mathbf{2c})}$	$\frac{Z\text{-}(\mathbf{2c})}{E\text{-}(\mathbf{2c})}$
0.1			0.286	0.21	0.205	0.22	0.156	0.20			0.075	0.20
0.15	0.833	0.30	0.501	0.25	0.388	0.24	0.338	0.24	0.234	0.23	0.188	0.23
0.20	1.09	0.35	0.684	0.28	0.555	0.27	0.495	0.26	0.412	0.26	0.293	0.25
0.30	1.23	0.37	1.07	0.34	0.944	0.34	0.829	0.32	0.725	0.31	0.570	0.29
0.40	1.44	0.40	1.29	0.37	1.17	0.37	1.06	0.36	0.944	0.35	0.844	0.33
0.60	1.65	0.44	1.54	0.43	1.47	0.41	1.35	0.41	1.23	0.39	1.16	0.39
1.0	1.90	0.49	1.80	0.48	1.72	0.47	1.63	0.46	1.51	0.45	1.48	0.46
2.0	2.05	0.53	1.95	0.52	1.98	0.51	1.69	0.46	1.65	0.50	1.67	0.49

Table 3. Product distribution in the photolysis of diazirine (**1d**) and MeOH in benzene

T/°C	4.0		11.7		19.2		26.4	
[MeOH]/M	$\frac{(\mathbf{3d})}{(\mathbf{2d})}$	$\frac{Z\text{-}(\mathbf{2d})}{E\text{-}(\mathbf{2d})}$	$\frac{(\mathbf{3d})}{(\mathbf{2d})}$	$\frac{Z\text{-}(\mathbf{2d})}{E\text{-}(\mathbf{2d})}$	$\frac{(\mathbf{3d})}{(\mathbf{2d})}$	$\frac{Z\text{-}(\mathbf{2d})}{E\text{-}(\mathbf{2d})}$	$\frac{(\mathbf{3d})}{(\mathbf{2d})}$	$\frac{Z\text{-}(\mathbf{2d})}{E\text{-}(\mathbf{2d})}$
0.10	0.115	0.07	0.0763	0.10	0.0520	0.09	0.0362	0.11
0.15	0.285	0.08	0.171	0.08	0.0958	0.09	0.0746	0.10
0.20	0.510	0.09	0.285	0.09	0.164	0.09	0.147	0.10
0.30	0.712	0.12	0.372	0.11	0.315	0.09	0.212	0.10
0.40	1.04	0.10	0.802	0.08	0.402	0.09	0.328	0.10
0.60	1.32	0.08	1.24	0.09	0.643	0.09	0.544	0.09

Excellent linear correlation was obtained, however, when styrene:acetal ratios were plotted against $1/[\mathrm{ROH}]^2$, with correlation coefficients >0.99. Typical plots are shown in Figure 3. The results can be interpreted in terms of a kinetic model in which the singlet benzylchlorocarbene[5] can react with two alcohol molecules contained in the oligomer chain, leading to a reversibly formed complex (ylide) which can subsequently react to form the acetal or chlorostyrene. The carbene can also give rise to the chlorostyrene directly by 1,2-H shift as shown in the Scheme. It is noted that two routes (k_i and k_i') are included for the production of chlorostyrene in order to account for the stereochemistry of chlorostyrene formation in the reaction. Equation (2) gives the concentration

$$[\text{complex}] = \frac{k_1[\mathrm{MeOH}]^2[\mathrm{C}\!:]}{k_{-1} + k_i' + k_2} \qquad (2)$$

of the complex. The rate of acetal formation is given by (3), and the rate of chlorostyrene formation by (4). Thus, the relative rate for chlorostyrene and acetal formation could best be represented by combining equations (3) and (4) to give (5)

$$\frac{\mathrm{d}[\text{acetal}]}{\mathrm{d}t} = \frac{k_1 k_2[\mathrm{MeOH}]^2[\mathrm{C}\!:]}{k_{-1} + k_i' + k_2} \qquad (3)$$

$$\frac{\mathrm{d}[\text{chlorostyrene}]}{\mathrm{d}t} = [\mathrm{C}\!:]k_i + \frac{k_i' k_1[\mathrm{MeOH}]^2}{k_{-1} + k_i' + k_2} \qquad (4)$$

where relationship (6) holds. Equation (5) predicts an inverse

$$\frac{\text{chlorostyrene}}{\text{acetal}} = \frac{k_i}{k_t}\frac{1}{[\mathrm{MeOH}]^2} + \frac{k_i'}{k_2} \qquad (5)$$

$$k_t = \frac{k_1 k_2}{(k_{-1} + k_i' + k_2)} \qquad (6)$$

second-order dependence of chlorostyrene:acetal ratio on the alcohol concentration. Values for k_i/k_t and k_i'/k_2 (Table 6) were derived from the slopes and intercepts of plots similar to those in Figure 3. The ratios of k_i/k_2 are insensitive to temperature changes for chlorocarbene–alcohol reactions, suggesting that $E_i' = E_2$. However, in the bromocarbene–methanol reaction these ratios increase with increasing temperature. Hence $E_i' > E_2$, and the formation of bromostyrene from the complex is therefore not important.

Temperature dependence of k_i/k_t (Figure 4) provides the values for $E_i - E_t$ and $\Delta S_i^\ddagger - \Delta S_t^\ddagger$ (Table 7). The observed linearity for all the Arrhenius plots requires that $k_1 k_2/k_{-1} + k_2 + k_i'$ be reduced to $k_1 k_2/k_{-1}$. Had equation (6) not been

Table 4. Product distribution in the photolysis of diazirine (**1a**) and EtOH in benzene

T/°C	5.0		10.1		15.1		20.1		25.0		30.1	
[EtOH]/M	(**3e**)/(**2a**)	Z-(**2a**)/E-(**2a**)	(**3e**)/(**2a**)	Z-(**2a**)/E-(**2a**)	(**3e**)/(**2a**)	Z-(**2a**)/E-(**2a**)	(**3e**)/(**2a**)	Z-(**2a**)/E-(**2a**)	(**3e**)/(**2a**)	Z-(**2a**)/E-(**2a**)	(**3e**)/(**2a**)	Z-(**2a**)/E-(**2a**)
0.10	0.277	0.24	0.220	0.24	0.172	0.24	0.125	0.23	0.105	0.24	0.0818	0.24
0.15	0.499	0.27	0.421	0.27	0.340	0.27	0.263	0.26	0.227	0.26	0.177	0.26
0.20	0.679	0.30	0.583	0.29	0.495	0.29	0.427	0.28	0.365	0.28	0.289	0.27
0.30	1.00	0.34	0.865	0.34	0.791	0.33	0.716	0.33	0.621	0.32	0.498	0.31
0.40	1.20	0.37	1.08	0.37	0.955	0.35	0.899	0.36	0.816	0.35	0.714	0.34
0.60	1.51	0.42	1.32	0.40	1.29	0.40	1.18	0.40	1.09	0.39	1.00	0.38

Table 5. Product distribution in the photolysis of diazirine (**1c**) with ethylene glycol in nitromethane

T/°C	13.8		19.8		25.0		31.5	
[EG]/M	(**3f**)/(**2c**)	Z-(**2c**)/E-(**2c**)	(**3f**)/(**2c**)	Z-(**2c**)/E-(**2c**)	(**3f**)/(**2c**)	Z-(**2c**)/E-(**2c**)	(**3f**)/(**2c**)	Z-(**2c**)/E-(**2c**)
0.1	0.694	0.32	0.576	0.34	0.510	0.33	0.383	0.25
0.15	0.900	0.34	0.775	0.35	0.696	0.35	0.560	0.33
0.20	1.09	0.35	0.948	0.37	0.861	0.36	0.718	0.35
0.25	1.21	0.37	1.10	0.39	1.07	0.38	0.872	0.37
0.33	1.36	0.38	1.32	0.41	1.19	0.40	1.00	0.39
0.40	1.40	0.39			1.42	0.40	1.12	0.35
0.60	1.94	0.43	1.85	0.45	1.80	0.43	1.58	0.42

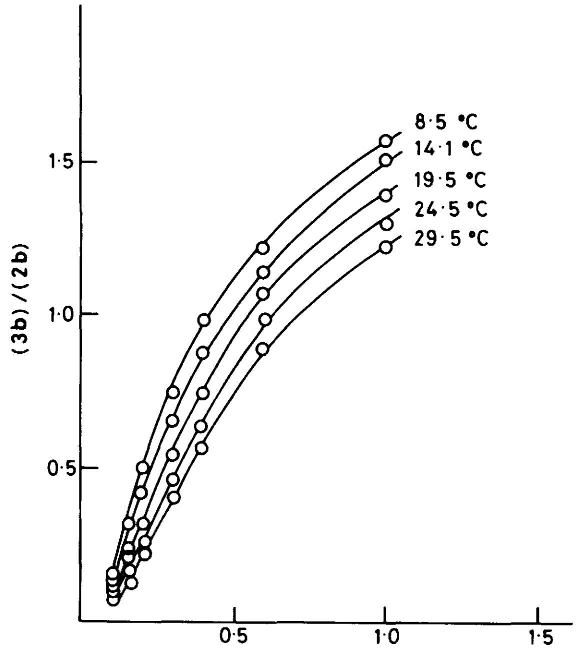


Figure 1. Plot of (**3b**)/(**2b**) *versus* [MeOH] in the reaction of (**1b**) with methanol

reduced to k_1k_2/k_{-1}, the Arrhenius law could not have applied. The values for k_i'/k_2 can be evaluated from the intercept of equation (5) and are found to be in the range 0.1—0.7. Thus $k_i' \simeq k_2$ and k_{-1} must be much greater than k_i' and k_2. These results are consistent with the formation of a reversibly formed complex as suggested in the Scheme.

The behaviour of methanol and ethanol in their reaction with chlorocarbene has been investigated. Both alcohols show inverse second-order kinetic dependence (Figure 3 and 5), a non-zero extrapolation for low alcohol concentration, and comparable activation parameters. Therefore, it is likely that the reactions of chlorocarbene with methanol and ethanol are similar.

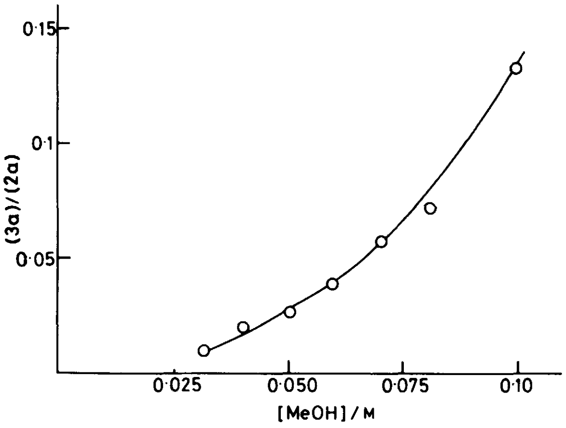


Figure 2. Plot of (**3a**)/(**2a**) *versus* [MeOH] at low methanol concentration. T 19.5 °C; [(**1a**)] 0.005M

The effects of substituents in the aryl group are reflected by the decreasing values of k_i/k_t in the order of p-MeO > p-Me > H > p-Cl.*[10] Thus electron-releasing group favours rearrangement while electron-withdrawing group facilitates insertion. The Hammett plot for log (k_i/k_t) *versus* σ^+ at 25 °C[10] gave a linear relationship with ρ -0.81.[10a] This reaction constant is similar to a ρ value of -0.70 computed for the reaction of benzylchlorocarbene with 2-methylpent-3-ene.[9]

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* The k_i/k_t value for p-$CH_3OC_6H_4CH_2\ddot{C}Cl$ in CH_3OH has been determined only at 25 °C and is 0.417.

Table 6. Ratios of k_i'/k_2 and k_i/k_t for benzylhalogenocarbene-alcohol reaction

	(**1a**) + MeOH			(**1a**) + EtOH			(**1b**) + MeOH			(**1c**) + MeOH			(**1d**) + MeOH			(**1c**) + EG	
T/°C	$\frac{k_i'}{k_2}$	$\frac{k_i}{k_t}$	T/°C	$\frac{k_i'}{k_2}$	$\frac{k_i}{k_t}$	T/°C	$\frac{k_i'}{k_2}$	$\frac{k_i}{k_t}$	T/°C	$\frac{k_i'}{k_2}$	$\frac{k_i}{k_t}$	T/°C	$\frac{k_i'}{k_2}$	$\frac{k_i}{k_t}$	T/°C	$\frac{k_i'}{k_2}$	$\frac{k_i}{k_t}$
5.0	0.69 ±0.12	0.0239 ±0.003	5.0	0.65 ±0.03	0.0298 ±0.001	8.5	0.60 ±0.04	0.0594 ±0.001	0.6	0.56 ±0.03	0.0150 ±0.001	4.0	0.31 ±0.19	0.0814 ±0.004	13.8	0.402 ±0.029	0.105 ±0.005
10.9	0.67 ±0.05	0.0388 ±0.001	10.1	0.70 ±0.03	0.0386 ±0.001	14.1	0.60 ±0.04	0.0832 ±0.001	8.9	0.59 ±0.94	0.0298 ±0.001	11.7	0.63 ±0.22	0.124 ±0.005	19.8	0.325 ±0.015	0.143 ±0.003
15.3	0.71 ±0.06	0.0489 ±0.002	15.1	0.69 ±0.02	0.0512 ±0.001	19.5	0.53 ±0.12	0.114 ±0.003	15.1	0.58 ±0.03	0.0436 ±0.001	19.2	1.42 ±0.30	0.182 ±0.007	25.0	0.296 ±0.023	0.168 ±0.004
19.9	0.70 ±0.06	0.0687 ±0.002	20.1	0.59 ±0.04	0.0736 ±0.001	24.5	0.54 ±0.12	0.148 ±0.003	20.1	0.55 ±0.03	0.0579 ±0.001	26.4	1.23 ±0.35	0.264 ±0.008	31.5	0.302 ±0.057	0.226 ±0.010
25.0	0.65 ±0.04	0.0921 ±0.001	25.0	0.61 ±0.05	0.0884 ±0.001	29.5	0.65 ±0.05	0.176 ±0.001	25.0	0.54 ±0.05	0.0817 ±0.002						
30.0	0.60 ±0.13	0.122 ±0.003	30.1	0.66 ±0.05	0.115 ±0.001				30.0	0.38 ±0.14	0.126 ±0.004						

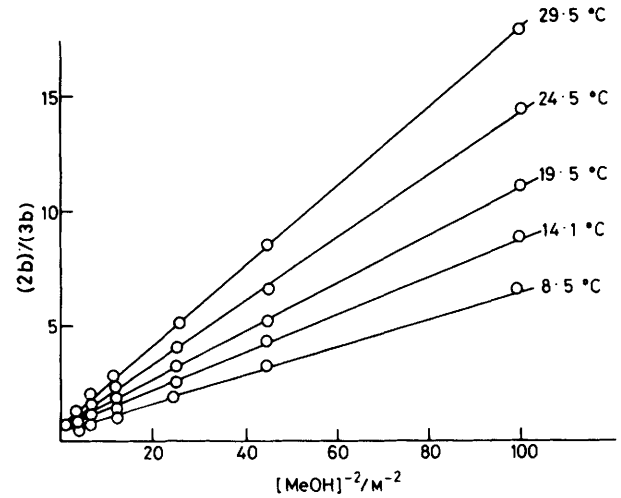
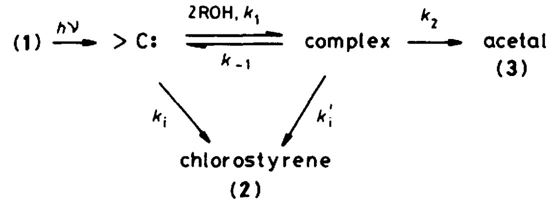


Figure 3. Plot of (**2b**)/(**3b**) *versus* 1/[MeOH]^2



Scheme.

Table 7. Activation parameters for benzylhalogenocarbene–alcohol reactions

Reaction	$E_i - E_t$/kcal mol^{-1}	A_i/A_t	$\Delta S_i^\ddagger - \Delta S_t^\ddagger$/ cal K^{-1} mol^{-1}
(**4a**) + MeOH	10.9 ± 0.3	$10^{6.9}$	31.6
(**4b**) + EtOH	9.2 ± 0.3	$10^{5.7}$	26.1
(**4b**) + MeOH	8.9 ± 0.4	$10^{5.7}$	26.1
(**4c**) + MeOH	11.5 ± 0.4	$10^{7.4}$	33.9
(**4d**) + MeOH	8.6 ± 0.1	$10^{5.7}$	26.1
(**4c**) + EG	7.4 ± 0.4	$10^{4.6}$	21.0

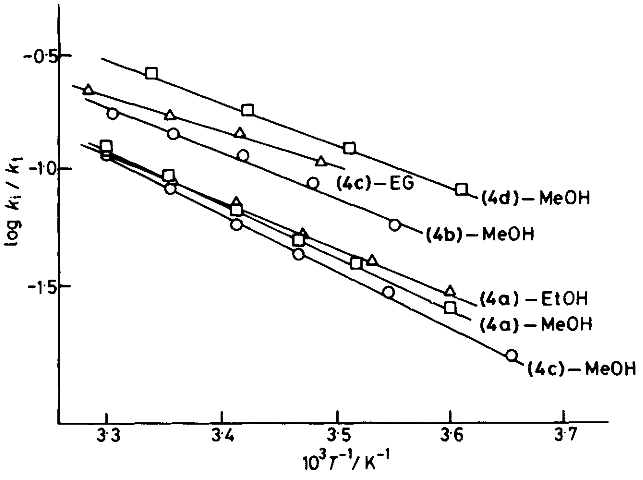


Figure 4. Arrhenius plots for the reactions of halogenocarbenes with alcohols

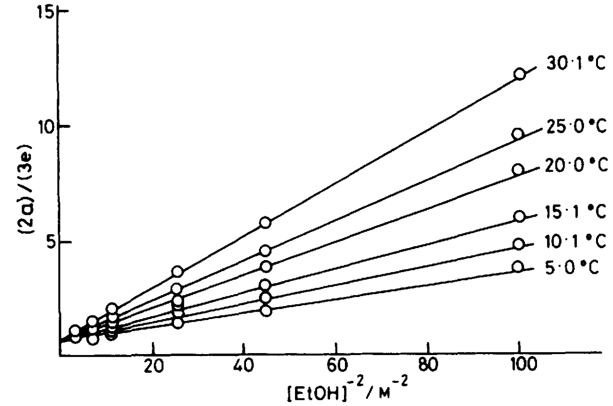


Figure 5. Plot of (**2a**)/(**3e**) *versus* 1/[EtOH]^2 in the reaction of (**1a**) with ethanol

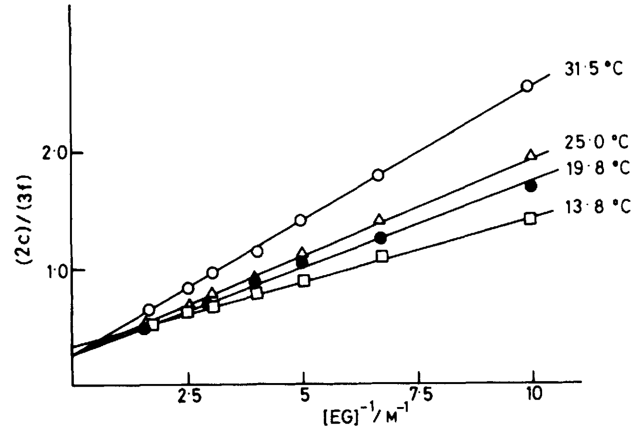


Figure 6. Plot of (**2c**)/(**3f**) *versus* 1/[Ethylene glycol]

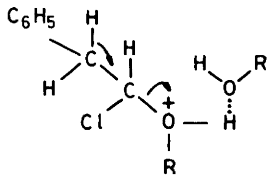
Since ρ for a 1,2-H shift will be negative, the reaction constant for the chlorocarbene reaction with alcohol or olefin can be expected to be very small and positive. This prediction is consistent with the large ρ value (+1.5) determined for chlorophenylcarbene–tetramethylethylene reaction where substituents can be in direct conjugation with the carbenic centre,[11] which is not possible in the present system.

Examination of Table 7 reveals that the difference in activation energies, $E_i - E_t$, for the reaction of (**1a**—**c**) with methanol is in the order *p*-Cl > H > *p*-Me. This fact, coupled with the observed trend of substituent effects on k_i/k_t, indicates the development of positive charge in the transition state for 1,2-migration and/or interaction of substituent with a developing negative charge in the insertion process. In all cases, $E_i - E_t$ is *ca.* 8.6—11.5 kcal mol^{-1}. The differences in the entropies of activation between the two competing reactions, $\Delta S_i^\ddagger - \Delta S_t^\ddagger$, are positive and range over 26.1—33.9 cal K^{-1} mol^{-1}. Since k_i(**4a**) = $10^{12.2}$exp − (6400/RT cal mol^{-1}) s^{-1},[12] all E_t values will likely be negative [*e.g.* the E_t(**4a**) is −4.5 kcal mol^{-1}][5] and since $\Delta S_i^\ddagger$ is *ca.* −2.6 cal K^{-1} mol^{-1}, $\Delta S_t^\ddagger$ will be largely negative. These results provide evidence that there is a large decrease in entropy for the insertion process; the near zero or negative activation energies point to the fact that a multi-step mechanism is involved in the formation of acetal.

Comparison of activation energies for the reactions (**4a** and **d**) shows that $(E_i - E_t)_{(4a)} > (E_i - E_t)_{(4d)}$ by 2.3 kcal mol^{-1}. The effect of substituting bromine for chlorine in (**4a**) is thus found to decrease E_i and/or increase E_t. This trend can be rationalized on the basis that bromine stabilizes the developing positive charge in the transition state for 1,2-migration more than chlorine since its bridging ability is greater than that of chlorine.[13] On the other hand, the developing negative charge in the transition state for the insertion reaction will be relatively destabilized by bromine since its electron-withdrawing ability is lower than that of chlorine. Hence, the 1,2-H-migration in (**4d**) is favoured and insertion is retarded. MNDO investigation of singlet carbene has shown that the 1,2-H shift in chlorocarbene is more favourable than that in fluorocarbene.[14] Similarly, 1,2-H-shift in bromocarbene would be more favourable than in chlorocarbene. This is consistent with our observation.

The kinetics of the reaction of (**1c**) with ethylene glycol was investigated to explore the nature of chlorocarbene reaction with an alcohol containing two OH functional groups. The products of the reaction were *p*,β-dichlorostyrene (**2c**) and 3-*p*-chlorobenzyl-1,3-dioxolane (**3f**). The dependence of styrene:dioxolane product ratio (Table 5) on glycol concentration was found to be inverse first order (Figure 6). The observation of first-order kinetics in ethylene glycol confirms that, in the reaction of methanol, two alcohol molecules may be involved in the rate-determining step.

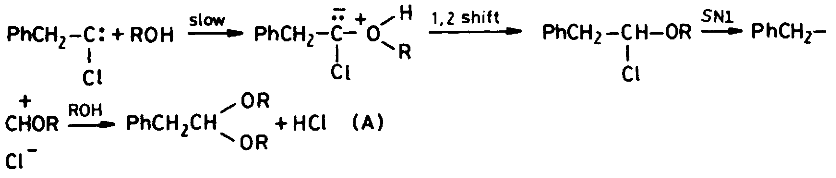
Mechanisms (A)—(E) for the insertion can be envisaged:



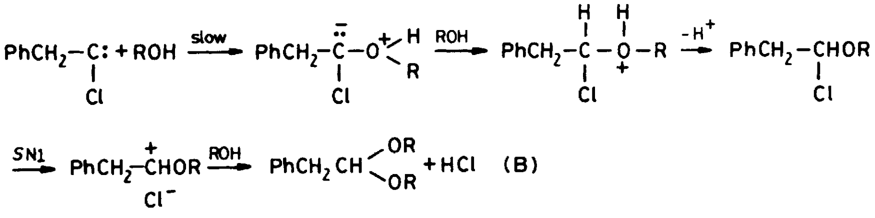
(IV)

Mechanisms (A) and (B) involve the interaction of the carbene with unassociated alcohol. In mechanism (A), the electrophilic attack of carbene on alcohol gives rise to an ylide which undergoes hydrogen transfer to yield an ether. Nucleophilic substitution by another alcohol molecule results in the acetal. Mechanism (B) is similar to (A) except that the ylide is transformed into the chloro ether through a protonated intermediate. Mechanism (C) indicates that a very rapid pre-equilibrium is established which is followed by a slow conversion of the complex to acetal. Both mechanisms (D) and (E) show the participation of associated alcohol. In (D), carbene reacts with hydrogen-bonded alcohol dimer to produce an ylide which leads to the chloro ether through a five-membered transition state followed by S_N1 reaction.

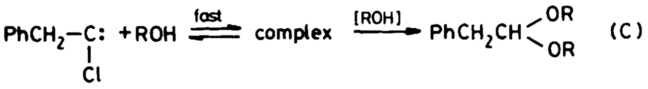
In mechanism (E), the ylide intermediate (I) which is formed



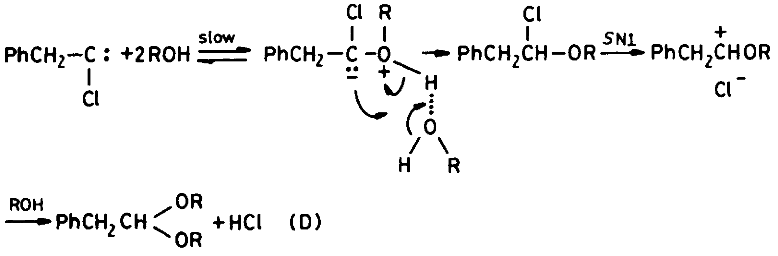
(A)



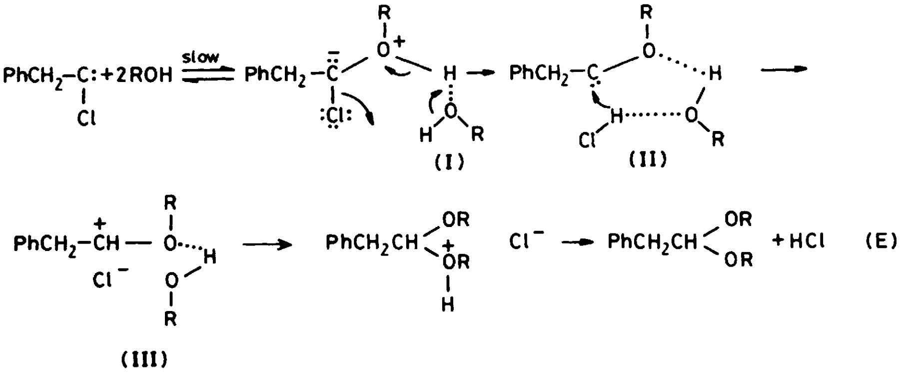
(B)



(C)



(D)



(E)

in a possibly reversible step gives rise to an alkoxycarbene (**II**) *via* a six-membered cyclic transition state. Protonation of this carbene by the HCl moiety leads to a carbocation (**III**) which then reacts with another molecule of ROH, giving the required acetal.

Mechanisms (A) and (B) are not likely since the kinetics are second order in alcohol and the formation of the ylide is most probably the rate-determining step. The proposal of a slow ylide formation is reasonable in view of the small solvent isotope effect (k_H/k_D 1.2) observed for the reaction of phenylchlorocarbene with methanol under laser photolysis at ambient temperature.[15] Although mechanism (C) may fit the second-order kinetic requirement, it would require the formation of a rapid pre-equilibrium, and a slow conversion of the complex to acetal. This does not appear to be consistent with the small solvent isotope effect observed for phenylchlorocarbene. It is obvious that detailed study on isotope effect is envisaged. Mechanisms (D) and (E) are more probable since they involve hydrogen-bonded dimers in the slow step. We favour mechanism (E) since the hydrogen-transfer process in the six-membered intermediate (**I**) is aided by the associated alcohol as well as by the loss of Cl^- from the electron-rich carbanion.

Further evidence for the intermediacy of an adduct in the insertion process can be obtained from the dependence of the stereochemistry of the chlorostyrene formation. As [ROH] increases, the *Z*:*E* ratio of chlorostyrene increases. This is most likely due to the existence of two routes by which chlorostyrene can be formed as shown in the Scheme. Because of steric effects the carbene conformer leading to the *E*-isomer of chlorostyrene is preferentially trapped[16] by alcohol to yield an adduct (**I**). Protonation of the adduct [*cf.* mechanism (E)] can give species (**IV**) which can undergo elimination to give chlorostyrene.

In the reaction of (**1d**) it was found that the methanol concentration has no effect on the stereochemistry of bromostyrene formation. The reactivity of the carbene conformers towards alcohol leading to *E*- and *Z*-isomers may be comparable resulting in the observed insensitivity of bromostyrene stereochemistry.

Reactions of carbenes with alcohols in rigid matrix at low temperature have received considerable attention.[17] Most work has been focused on reaction of arylcarbenes with triplet ground states and only recently have the temperature and matrix effects on the reactions of some singlet carbenes with ethanol been examined.[18] To gain further insight into the mechanism of O–H insertion, diazirines (**1a** and **d**) (0.01M) were photolysed in the presence of excess of methanol from room temperature to −210 °C. The relative yields of the products for the above reactions are summarized in Table 8. It is evident from Table 8 that there are a number of important trends. First, the behaviour of benzylbromocarbene is similar to benzylchlorocarbene with respect to its relative reactivity in their inter- and intra-molecular reactions. The yields of olefinic products resulting from intramolecular 1,2-H-shift decrease whereas the yield for intermolecular products increases over the 10 to −78 °C temperature range. The ratio for intramolecular–intermolecular (H–insertion) product reaches a minimum at *ca.* −78 °C and gradually increases again as the temperature is further lowered, thus giving rise to a V-shaped Arrhenius relationship.

When the environment becomes solid (< −100 °C), the trend is reversed. The H:insertion ratio increases. This behaviour is explicable by a change in rate-determining step as the temperature is lowered. Thus, the conversion of ylide (**I**) to carbene (**II**) may become the rate-limiting step.

It may be seen from Table 8 that the stereochemistry of 1,2-migration is sensitive to temperature as well as matrix effect. Thus, the ratio *Z*-(**2**):*E*-(**2**) is increasing when the temperature is lowered. As the temperature decreases the steric effects of N_2 present in the environment becomes important. The relative amount of the conformer leading to the *E* isomer decreases as a result of repulsion between the N_2 and the Ph group due to the lack of diffusibility.

Table 8. Product distribution for low-temperature photolysis

Photolysis of (**1a**) in MeOH							
T/°C	9.9	−12	−30	−78	−90	−196	−210
(**2a**)/(**3a**)	0.55	0.44	0.36	0.27	0.30	1.9	2.4
Z-(**2a**)/*E*-(**2a**)	0.56	0.63	0.71	0.81	0.82	1.1	1.1
Photolysis of (1d) in MeOH							
T/°C	11.8	1.0	−30	−63	−78	−130	−196
(**2d**)/(**3a**)	0.71	0.67	0.71	0.48	0.40	0.48	0.55
Z-(**2d**)/*E*-(**2d**)	0.10	0.08	0.35	0.54	0.40	0.43	0.38

Experimental

The n.m.r. spectra were recorded on a Varian T-60 and a Nicolet 360 spectrometer. G.l.c. analyses of relative yields of products were performed on a Varian Vista 6000 gas chromatograph fitted with a 6 ft × 2 mm (i.d.) glass column packed with CSP-20M and using the flame ionization detector. Peak areas were integrated with a Hewlett–Packard 3390 A recorder.

Irradiation was carried out with a 275 W GE sunlamp until all the diazirine (0.01M in all runs) was destroyed. Temperature control was within ±0.1 °C. A CS-052 filter was used to allow transmission of wavelength >350 nm. Low-temperature photolysis was carried out with slush baths using mixtures of organic solvents and liquid nitrogen.[19] The temperature of −210 °C was achieved by using solid nitrogen.

Benzene was shaken with concentrated sulphuric acid to remove thiophene, washed with water, dried over 4A molecular sieves, and distilled over calcium hydride. Methanol and ethanol were refluxed with magnesium and iodine for 12 h and distilled. The halogenodiazirines were synthesized from the benzylamidine precursors by oxidation with NaOCl or NaOBr.[8]

Products were identified by comparing the measured n.m.r. spectra with authentic samples or those reported in the literature.

Photolysis of 3-*Chloro*-3-*benzyldiazirine* (**1a**) *in* MeOH.—A solution of (**1a**) (0.5 g, 3.0×10^{-3} mol) in MeOH (10 ml) was photolysed at 20.0 °C for 10 h. The solvent was removed and the crude product was chromatographed on silica gel (30 g) eluting with 95:5 pentane–diethyl ether. Two fractions were collected. The first (0.124 g) was a mixture of *Z*- and *E*-β-chlorostyrene, δ 7.38 (Ph), 6.63 and 6.78 (ABq, *E*-olefinic H), and 6.08 and 6.63 (ABq, *Z*-olefinic H).[20] The second fraction contained phenylacetaldehyde dimethyl acetal (0.311 g),[21] δ 7.16 (s, 5 H), 4.45 (t, 1 H), 3.23 (s, 6 H), and 2.80 (d, 2 H). The overall product yield was 92%.

Photolysis of 3-*Chloro*-3-*benzyldiazirine* (**1a**) *in* EtOH.—A solution of (**1a**) (0.4 g, 2.4×10^{-3} mol) in EtOH (10 ml) was irradiated at 20.0 °C for 10 h. The solvent was removed and the product mixture was chromatographed as before. A mixture of *Z*- and *E*-β-chlorostyrene (0.11 g) and phenylacetaldehyde diethyl acetal (0.252 g), δ 7.13 (s, 5 H), 4.55 (t, 1 H), 3.50 (m, 4 H), 2.87 (d, 2 H), and 1.16 (t, 6 H), was obtained. The yield of products was 88%.

Photolysis of 3-*Chloro*-3-p-*methylbenzyldiazirine* (**1b**) *in* MeOH.—Compound (**1b**) (0.2 g, 1.1×10^{-3} mol) and MeOH (1.0 g) were dissolved in benzene (10 ml) and irradiated for 16 h at 10.0 °C. Solvent was removed and the residue chromatographed as before. *p*-Methyl-β-chlorostyrene (0.08 g), δ 7.0—7.1 (Ph), 6.09 (*cis*, H_α), 6.48 (*cis*, H_β), 6.46 (*trans*, H_α), and 6.68 (*trans*, H_β),[22] and *p*-methylphenylacetaldehyde dimethyl acetal (0.075 g), δ 7.03 (s, 4 H), 4.49 (t, 1 H), 3.30 (s, 6 H), 2.84 (d, 2 H), and 2.31 (s, 3 H), were obtained. The yield of products was 85%.

Photolysis of 3-*Chloro*-3-p-*chlorobenzyldiazirine* (**1c**) *in* MeOH.—A mixture of (**1c**) (0.42 g, 2.1 × 10^{-3} mol) and MeOH (1.0 g) was dissolved in benzene (15 ml) and irradiated at 10.0 °C for 16 h. The mixture was concentrated and the residue was chromatographed as described previously. *p*,β-Dichlorostyrene (0.141 g), δ 7.01—7.22 (Ph), 6.13 (*cis*, H_α), 6.44 (*cis*, H_β), 6.48 (*trans*, H_α), and 6.63 (*trans*, H_β),[22] and *p*-chlorophenylacetaldehyde dimethyl acetal (0.215 g), 7.10—7.26 (m, 4 H), 4.49 (t, 1 H), 3.30 (s, 6 H), and 2.87 (d, 2 H), were obtained. The overall product yield was 90%.

Photolysis of 3-*Bromo*-3-*benzyldiazirine* (**1d**) *in* MeOH.—Compound (**1d**) (0.3 g, 1.4 × 10^{-3} mol) in MeOH (5 ml) was irradiated for 10 h at 20.0 °C. The solvent was removed and the products separated by silica gel column as before. The first fraction from the column was a mixture of *Z*- and *E*-β-bromostyrene (0.161 g), δ 7.06 (Ph), 6.53 and 6.98 (ABq, *E*-olefinic H), and 6.30 and 6.92 (ABq, *Z*-olefinic H).[20] The second was phenylacetaldehyde dimethyl acetal (0.063 g). The product yield was 89%.

Photolysis of (**1c**) *in Ethylene Glycol*.—Compound (**1c**) (0.5 g, 2.5 × 10^{-3} mol) and ethylene glycol (1.5 g, 2.5 × 10^{-2}) in nitromethane (20 ml) were irradiated at 10 °C for 20 h. The solvent was removed and the residue was chromatographed on silica gel as before. The first fraction was a mixture of *p*,β-dichlorostyrene (220 mg). The second fraction contained 2-*p*-chlorobenzyl-1,3-dioxolane (145 mg), δ 7.21 (s, 4 H), 2.85 (d, 2 H), 5.68 (t, 1 H), and 3.95 (s, 4 H). The product yield was 88%.

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