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Termolecular Trapping of Benzylchlorocarbene by Methanol

Michael T. H. Liu* and Ramasamy Subramanian

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

The trapping of benzylchlorocarbene by methanol is termolecular leading to a frequency factor of 2×10^5 l^2 mol^{-2} s^{-1} and an activation energy of -4.5 kcal mol^{-1} (18.8 kJ mol^{-1}).

The reactions of carbenes with alcohols have received considerable attention.[1] The laser photolysis experiments of Griller, Liu, and Scaiano[2] have demonstrated that chlorocarbenes can have a strong discrimination in their reactivity towards the monomers and oligomers of various alcohols. As part of our continuing efforts to understand the chemistry of the carbenes generated from diazirines,[3] we report unusual kinetic behaviour for the reactions of singlet benzylchlorocarbene† with methanol.

3-Benzyl-3-chlorodiazirine (**1**) was synthesized by Graham's method[4] and 0.0210 M solutions in benzene were irradiated (CS-052 filter) at 5—30 °C in the presence of various concentrations of methanol (0.1—2.4 M) such that the alcohol was always in excess (Table 1). The products‡ were *E*- and *Z*-chlorostyrene (**2**), HCl, and phenylacetaldehyde dimethyl acetal (**3**) according to Scheme 1.

The photochemically generated benzylchlorocarbene (**4**) can give rise, by two competing reactions, to the chlorostyrenes by an intramolecular 1,2-shift *or* react with methanol leading to the formation of the acetal (**3**).

The formation of the product (**3**) raises several interesting mechanistic possibilities. (i) The carbene (**4**) reacts with an

† Irradiation of (**1**) at 4 K produced no detectable e.s.r. signal. We are grateful to Dr. K. F. Preston for carrying out these experiments. Addition of benzylchlorocarbene to (*Z*)-4-methylpent-2-ene is stereospecific (ref. 6b).

‡ Products were identified by n.m.r. and mass spectroscopic analysis and by comparison with spectra of authentic samples. Relative yields of products were analysed on a Varian VISTA 6000 g.c. instrument using a 6 ft × 2 mm (i.d.) glass column packed with CSP-20M. Peak areas were integrated by a HP 3390A recorder. The HCl produced in this reaction does not react with (**1**). Overall product balance shows that 95% of (**1**) can be accounted for in terms of (**2**) and (**3**). Control experiments indicate that the *Z*/*E* ratio in (**2**) is not affected by HCl.

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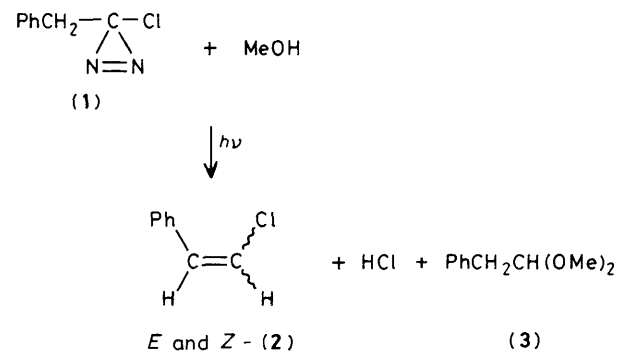
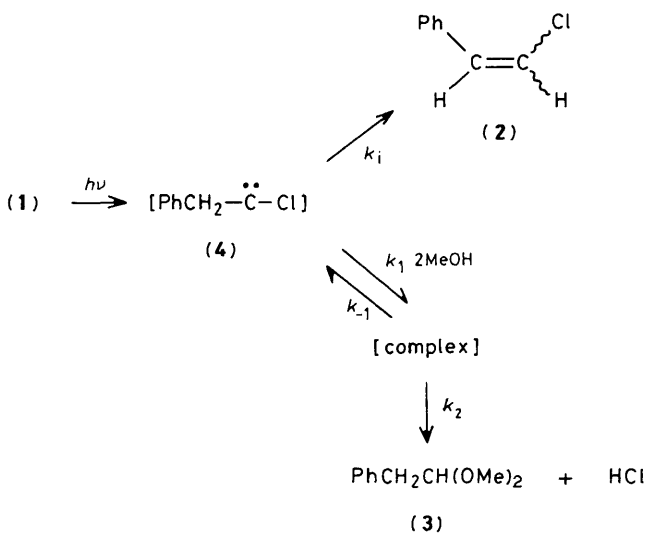
Table 1. Product distribution as a function of [MeOH] and temperature.

T/°C	5.0		10.9		13.0		15.3		19.9		25.0		30.0	
[MeOH]/M	(3)/(2)	Z/E[a]	(3)/(2)	Z/E	(3)/(2)	Z/E	(3)/(2)	Z/E	(3)/(2)	Z/E	(3)/(2)	Z/E	(3)/(2)	Z/E
0.10	0.356	0.34	0.221	0.25	0.211	0.25	0.180	0.25	0.132	0.25	0.101	0.24	0.0769	0.24
0.15	0.446	0.30	0.430	0.30	—	—	0.360	0.29	0.277	0.28	0.218	0.27	0.185	0.27
0.20	0.688	0.37	0.532	0.32	0.513	0.32	0.458	0.31	0.400	0.31	0.328	0.30	0.260	0.29
0.30	0.966	0.38	0.872	0.38	—	—	0.768	0.37	0.578	0.35	0.609	0.35	0.525	0.34
0.40	1.38	0.51	1.04	0.42	1.04	0.41	0.913	0.39	0.894	0.40	0.778	0.38	0.671	0.37
0.80	1.55	0.51	1.46	0.49	1.34	0.48	1.27	0.46	1.31	0.48	1.19	0.46	1.09	0.46
1.2	1.72	0.55	1.54	0.51	1.57	0.52	1.57	0.53	1.43	0.51	1.43	0.52	1.40	0.52
2.4	1.96	0.60	1.77	0.57	1.80	0.58	1.84	0.59	1.75	0.57	1.67	0.58	1.66	0.57
k_i/k_t[b]	0.0239(29)		0.0388(13)		0.0412(16)		0.0489(16)		0.0687(16)		0.0921(10)		0.122(3)	

[a] Z/E ratio for (2). [b] Standard deviations in parentheses.



Scheme 1



Scheme 2. The step for the direct decomposition of the complex to (2) should be included in this scheme. However, this will not alter any arguments presented or the kinetic parameters derived for A_t and E_t.

MeOH molecule to give a chloroether followed by nucleophilic substitution involving a second MeOH molecule to form (3). (ii) The carbene (4) reacts rapidly with two molecules of MeOH from the methanol oligomer chain to form (3).

If mechanisms (i) or (ii) were operative, the ratio of products from intermolecular and intramolecular reactions should vary linearly with methanol concentration, but plots of the observed change in the ratio (3)/(2) *vs.* [MeOH]^2 or [MeOH] showed pronounced deviations from linearity. However, linear regression analysis of the ratio (2)/(3) *vs.* 1/[MeOH]^2 gave correlation coefficients >0.99.

The results can be interpreted in terms of a kinetic model in which a complex is formed reversibly by the reaction of the carbene with two methanol molecules contained in the oligomer chain, as shown in Scheme 2.

Application of steady-state treatment to Scheme 2 leads to expression (1), where $k_t = k_1k_2/(k_{-1} + k_2)$.

$$\frac{(2)}{(3)} = \frac{k_i}{k_2} + \frac{k_i}{k_1k_2[1/(k_{-1}+k_2)][\mathrm{MeOH}]^2} = \frac{k_i}{k_2} + \frac{k_i}{k_t} \cdot \frac{1}{[\mathrm{MeOH}]^2} \quad (1)$$

Linear regression analysis gave the values for k_i/k_t in Table 1. The Arrhenius relationship leads to $E_i - E_t = 10.9 \pm 0.3$ kcal mol^{-1} and $A_i/A_t = 10^{6.9 \pm 0.2}$.§

Since the application of the Arrhenius law to k_i/k_t has a correlation coefficient greater than 0.99, it follows that $k_{-1} \gg k_2$ (*i.e.*, the complex is formed in a rapid equilibrium) and that k_t is a combination of an equilibrium constant K with a rate constant k_2, hence $E_t = \Delta H + E_2$. E_2 will be positive but the carbene–methanol association equilibrium will be exothermic, and ΔH will be negative. If $|\Delta H| > E_2$, then E_t will be negative. This is exactly what is observed. If the isomerization rate constant is taken to be[5] $k_i/\mathrm{s}^{-1} = 10^{12.2} \exp(-6400/RT)$, then A_t and E_t can be estimated to be 2×10^5 l^2 mol^{-2} s^{-1} and -4.5 kcal mol^{-1} respectively.¶

The observed second-order kinetics in methanol together with the low frequency factor and the negative activation energy provide convincing evidence that the reaction of the carbene and methanol is termolecular. The participation of the carbene (4) with two MeOH molecules in a singlet kinetic process may be reasonable in view of the proximity of the two MeOH molecules in the oligomer chain.

The increase in the Z/E ratio for (2) as a function of methanol concentration (Table 1) lends support to our proposal of the reversible formation of a complex. For steric reasons the conformation (I) of the complex which leads to Z-isomer is more stable than (II). The intervention of a reversibly formed dissociable intermediate has also been proposed in the addition of a carbene to alkenes.[6]

§ 1 cal = 4.184 J.

¶ The activation energy for the reaction of p-MeOC$_6$H$_4$–$\ddot{\mathrm{C}}$–Cl with MeOH determined by laser photolysis has been reported (ref. 2) to be -4.7 kcal mol^{-1}.

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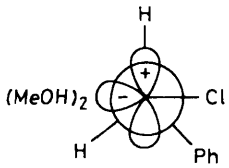
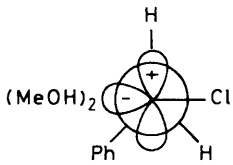


(I)



(II)

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