Benzylchlorocarbene: A New Ambiphile

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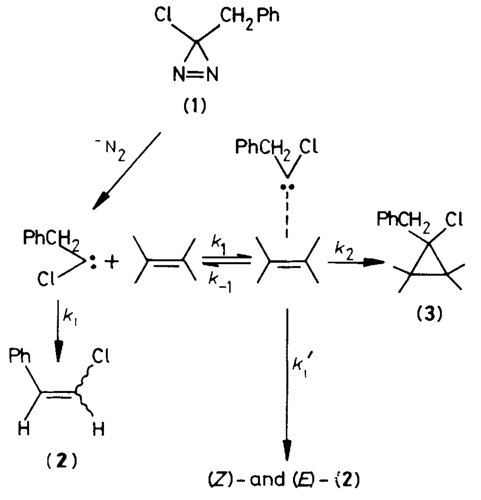
Relative reactivities of benzylchlorocarbene towards electron-poor and electron-rich alkenes indicate the carbene to be ambiphilic.

The reactions of chlorocarbenes with alkenes to form cyclopropanes have received considerable attention.[1] In the studies on volumes of activation for the cycloaddition of phenylchlorocarbene with alkenes, Turro, Moss, and coworkers suggested that their results are consistent with the reversibly formed carbene–alkene complex or the early one- or two-bond transition state.[2] Recent work on the addition of phenylchlorocarbenes to α,β-unsaturated systems indicates that the reaction occurs with remarkable ease.[3] Frontier Molecular Orbital (F.M.O.) analysis establishes the necessity

Table 1. Product distribution in photolysis and thermolysis.

[BVE]/	$h\nu$, 24.0 °C		Heat, 115.7 °C		[HEX]/	$h\nu$, 23.0 °C		[MES]/	$h\nu$, 23.6 °C		[ClACN]/	$h\nu$, 25.5 °C		Heat, 92.3 °C	
M	Z/E	(**3**)/(**2**)	Z/E	(**3**)/(**2**)	M	Z/E	(**3**)/(**2**)	M	Z/E	(**3**)/(**2**)	M	Z/E	(**3**)/(**2**)	Z/E	(**3**)/(**2**)
0.1	0.40	0.245	0.17	0.0180	0.1	0.30	0.0931	0.1	0.31	0.0840	0.2	0.39	0.637	0.15	0.190
0.2	0.39	0.462	0.17	0.0452	0.2	0.32	0.193	0.2	0.32	0.134	0.4	0.44	0.885	0.15	0.310
0.4	0.41	0.779	0.17	0.0993	0.5	0.32	0.450	0.4	0.33	0.201	0.8	0.52	1.090	0.16	0.468
0.8	0.45	1.180	0.17	0.178	0.8	0.33	0.592	0.8	0.33	0.253	1.2	0.50	1.196	0.16	0.585
1.2	0.47	1.412	0.17	0.253	1.1	0.35	0.746	1.2	0.33	0.233	1.6	0.55	1.324	0.17	0.683
1.6	0.50	1.515	0.17	0.325	1.4	0.36	0.905	1.6	0.32	0.279	2.0	0.55	1.237	0.17	0.766
2.0	0.52	1.706	0.17	0.384	1.7	0.37	0.943	2.0	0.31	0.281	2.4	0.65	1.449	0.17	0.799
2.5	0.54	1.712	0.17	0.446	2.0	0.40	1.032	2.5	0.32	0.275	2.8	0.65	1.449	0.18	0.815



Scheme 1

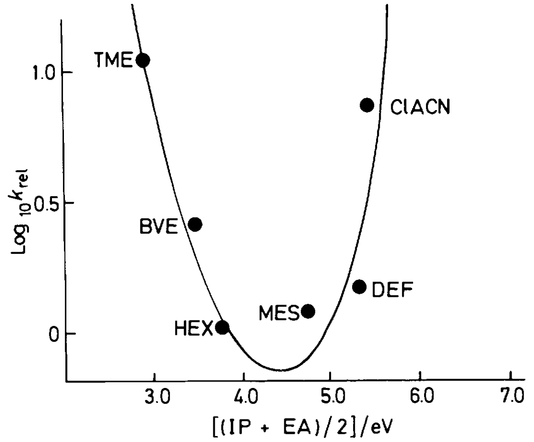


Figure 1. Log k_{rel} *vs.* 'π-molecular electronegativity' (IP + EA)/2.

of including a nucleophilic term in estimating the stabilization energy of the transition state for addition of these carbenes with electron deficient alkenes.[3] Also, the stereochemistry of the β-chlorostyrenes formed during the decomposition of 3-chloro-3-benzyldiazirine (**1**) is explained in terms of a carbene–alkene intermediate.[4] We now report the decomposition of the diazirine (**1**)[5] in the presence of various alkenes in an attempt to understand the philicity of benzylchlorocarbene.

Photolysis and thermolysis of 0.02 M of (**1**) in the presence of excess of alkene in iso-octane gave *E*- and *Z*-β-chlorostyrenes, (**2**), and cyclopropanes, (**3**) (Scheme 1). The alkene substrates used in the present experiments were n-butyl vinyl ether (BVE), hex-1-ene (HEX), diethyl mesaconate (MES), and α-chloroacrylonitrile (ClACN). The cyclopropanes/chlorostyrenes product ratios were determined as a function of temperature and alkene concentrations. In general, plots of (**3**)/(**2**) ratios *vs.* alkene concentrations show curvature for photolysis and less so for thermolysis. Representative data are given in Table 1. A mechanistic model proposed earlier[4] accounts not only for the curvature in (**3**)/(**2**) *vs.* [alkene] plots but also predicts the change in Z/E ratio of (**2**) with increase in alkene concentration.

Employing equation (1),[4] values for k_i/k_t were obtained by correlating (**2**)/(**3**) *vs.* 1/[alkene] data; k_t is the overall trapping rate constant and k_i is the rate constant for 1,2-H shift.

$$(\mathbf{2})/(\mathbf{3}) = (k_i/k_t)/[\text{alkene}] + k_i'/k_2 \qquad (1)$$

Table 2. Relative cyclopropanation rate constants at 25 °C.

	TME	BVE	HEX	MES	DEF	ClACN
k_{rel}	11	2.8	1	1.3	1.5	6.9
k_i/k_t	0.105	0.380	1.15	0.955	0.692	0.166

Least-squares analysis of log k_i/k_t *vs.* $1/T$ for various alkenes gave $E_i - E_t$ values of 8.1 ± 0.2, 6.6 ± 0.1, 6.8 ± 0.2, 6.3 ± 0.3, 5.4 ± 0.4, and 6.0 ± 0.4 kcal mol^{-1} (cal = 4.184 J) and A_i/A_t values of $10^{4.9}$, $10^{4.4}$, $10^{5.0}$, $10^{4.4}$, $10^{3.9}$, and $10^{3.6}$ for TME (tetramethylethylene),[7] BVE, HEX, DEF (diethyl fumarate),[6] MES, and ClACN respectively.

If E_i is taken[7] to be 6.4 kcal mol^{-1}, it can be seen that the activation energies for cycloaddition of Bz–$\ddot{\text{C}}$–Cl (benzylchlorocarbene) to alkenes are approximately zero kcal mol^{-1}, in agreement with the E_a obtained by laser flash photolysis for Ph–$\ddot{\text{C}}$–Cl with alkenes.[1,3,8]

Benzylchlorocarbene is generally regarded as an electrophilic carbene through its addition to alkenes. α-Chloroacrylonitrile was introduced by Moss, Krogh-Jespersen, and co-workers[9] as an excellent detector substrate for nucleophilic and ambiphilic carbenes. During this study, use of ClACN as a substrate has indicated that Bz–$\ddot{\text{C}}$–Cl is an ambiphilic carbene.

The relative cyclopropanation rate constants (k_{rel}), derived from k_i/k_t ratios, for Bz–$\ddot{\text{C}}$–Cl in iso-octane at 25 °C are in Table 2.

Simple explanations based on steric factors and decreasing electrophilic reactivity of benzylchlorocarbene towards increasingly electron-poor alkenes do not rationalize the present kinetic data. A better way[3] to relate reactivity rates with the nature of the alkene substrate is to plot log k_{rel} against the 'π-molecular electronegativity.' We define 'π-molecular electronegativity' of an alkene to be (IP + EA)/2, the average of its π and π* orbital energies as approximated by ionisation potential (IP) and electron affinity (EA) values. The resulting U-shaped plot (Figure 1) indicates that the rate increases at both ends where electrophilic [LUMO(carbene)/HOMO (alkene)] and nucleophilic [HOMO(carbene)/LUMO (alkene)] interactions become pronounced. A similar parabola was also observed for $Ph-\ddot{C}-Cl$.[3] It is now clear that benzylchlorocarbene, like phenylchlorocarbene,[3,8] can be induced to react rapidly as a nucleophile in the presence of electron-poor to react rapidly as a nucleophile in the presence of electron-poor alkenes. It may be seen from (Figure 1) that k_{rel} is highest for both TME (electron rich) and ClACN (electron poor), intermediate for BVE, and least for DEF, MES, and HEX.

In conclusion it may be said that benzylchlorocarbene is found to be generally ambiphilic in reactions with both electron-poor and electron-rich alkenes. Also, similar activation parameters for the two sets of electronically different alkenes vitiate any distinction between the benzylchlorocarbene reaction towards electron-rich and electron-poor alkenes.

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