

Photolysis of 3-Chlorodiazirine in the Presence of Alkenes: Orientational Factors in the Intermolecular Interception of Chlorocarbene by Alkenes

Hideo Tomioka,*^a Norihiro Hayashi,^a Yasuji Izawa,^a and Michael T. H. Liu^b

^aDepartment of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514 Japan

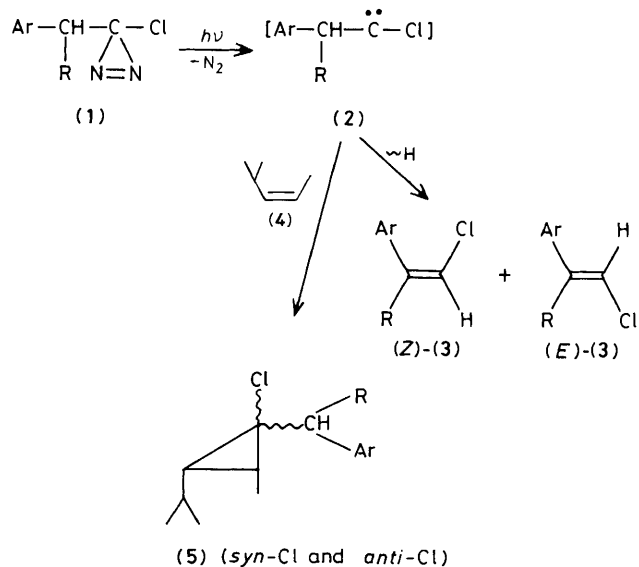
^bDepartment of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, Canada C1A 4P3

The stereochemistry of the 1,2-H shift of photolytically generated benzylchlorocarbene is significantly affected by aryl substituents and by the addition of an alkene.

Theoretical and synthetic interest has been shown in 1,2-hydrogen migration to divalent carbon generating an alkene and considerable efforts have been made to clarify the nature of the migration.¹⁻³ Prior to 1970, it was generally accepted⁴ that singlet carbenes with readily-accessible intramolecular reaction channels would not be efficiently trapped by external reagents. But since Moss and Mamantov⁵ found that methylchlorocarbene added to a variety of alkenes to give the expected cyclopropanes, several recent studies^{6,7} have dealt with the general problem of suppressing 1,2-hydrogen migration, thus providing important information on the effect of the multiplicity and structure of the carbene on its reaction with alkenes. However, in spite of the studies on the stereochemistry of cyclopropanation, little attention has been given to the stereochemical outcome of the carbene 1,2-hydrogen migration in the presence of external trapping reagents. We report here that intermolecular interception of these 'elusive' carbenes by an alkene has resulted in what appears to be a significant change in the stereochemistry of the intramolecular process.

Irradiation of 3-benzyl-3-chlorodiazirines (1)[†] in cyclohexane was carried out with a 300 W high-pressure Hg lamp at 10 °C until all the diazirine was destroyed. A Corning CS-052 filter cutoff at 350 nm was used in order to avoid product

[†] All chlorodiazirines (1) used in this study were prepared by Graham's method and purified by chromatography on silica gel before irradiation. The absence of styrenes before irradiation was confirmed by n.m.r. spectroscopy.



Scheme 1

	R	Ar
a	Me	Ph
b	H	4-MeOC ₆ H ₄
c	H	4-MeC ₆ H ₄
d	H	Ph
e	H	4-ClC ₆ H ₄
f	H	3,4-Cl ₂ C ₆ H ₃

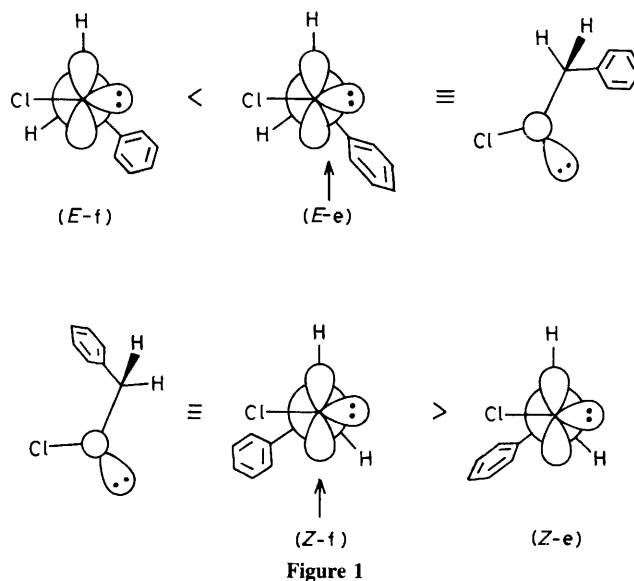
Table 1. Product distributions in the photolysis of (1) in (*Z*)-4-methylpent-2-ene (4)-cyclohexane.^a

(1)	[(4)]/[(1)]	Yield, % ^b					
		(<i>Z</i>)-(3)	(<i>E</i>)-(3)	(5) (Isomer ratio) ^c	<i>E/Z</i>	(5)/(3)	
a	0	20.7	73.2	—	3.5	—	
	100	18.9	64.1	7.2 (1.1)	3.4	0.09	
	500	16.8	56.1	17.5 (1.1)	3.3	0.24	
b	0	5.2	79.2	—	15.2	—	
	10	4.8	68.1	12.9 (18.0)	14.2	0.18	
	100	3.4	34.9	49.2 (24.9)	10.2	1.28	
	500	2.2	18.1	66.6 (24.1)	8.2	3.28	
	c	0	6.0	71.4	—	11.9	—
d	10	4.9	56.8	20.2 (13.4)	11.5	0.33	
	100	3.4	23.7	65.4 (15.0)	7.0	2.41	
	500	2.2	10.2	74.6 (12.1)	4.6	6.02	
e	0	10.9	62.3	—	5.7	—	
	10	8.7	43.6	28.9 (8.6)	5.0	0.55	
	100	5.7	15.6	72.0 (13.4)	3.1	3.48	
	500	3.8	8.1	76.7 (14.0)	2.1	6.45	
	f	0	10.6	56.5	—	5.3	—
f	10	8.7	39.3	31.4 (14.0)	4.5	0.65	
	100	5.3	17.1	71.2 (16.8)	3.2	3.18	
	500	4.7	11.8	77.1 (14.7)	2.5	4.67	
	f	0	8.5	46.1	—	5.4	—
	10	6.3	31.1	38.1 (16.3)	4.9	1.02	
100	4.7	18.0	70.4 (16.6)	3.8	3.10		
500	3.6	15.6	78.6 (25.2)	4.3	4.09		

^a Irradiations were performed on a 10 mm solution of the diazirine (1) in cyclohexane at 10 °C through a Corning CS-052 filter. Products were identified by g.l.c.–mass spectroscopic comparison with authentic samples and/or by structurally consistent i.r. and n.m.r. spectra. ^b Determined by g.l.c. and based on the amount of (1) used. The averages of duplicate runs are tabulated; reproducibility was $\pm 5\%$. ^c Ratio of two g.l.c. peaks corresponding to the cyclopropanes (5); the major isomer eluted first in a 4.0 mm \times 2.0 m column packed with 5% poly(ethylene glycol) 20 M on 60–80 mesh Uniport B.

isomerization. The photolysis products of (1) were (*Z*)- and (*E*)- β -chlorostyrenes (3), apparently arising from a 1,2-H shift in the photolytically generated chlorocarbene (2) (see Table 1). Inspection of the results in Table 1 indicates that the *E/Z* ratio of chlorostyrene is influenced by aryl substituents; the amount of (*E*)-olefin decreases as the ring substituents are changed from electron-donating to electron-withdrawing groups.

When the irradiation of (1) was carried out in the presence of the alkene (4), 1,2-H migration was considerably suppressed concomitant with the formation of the cyclopropanes (5)[‡] (see Table 1). An interesting result observed in Table 1 is that the intermolecular interception caused a significant change in the stereochemistry of the intramolecular reactions of the trapped carbenes. Thus, as the amount of cyclopropane (5) increased with the concentration of the external alkene, the *E/Z* ratio of the chlorostyrene decreased (Scheme 1).[§] The reason for this change is probably partly due to the difference in the reactivity of the carbene conformers towards alkenes. The mechanism of 1,2-H shift involves⁸ an electrophilic pull of hydride through the vacant p orbital of the singlet carbene, starting from the approximate carbene conformations *E* and *Z* (for the formation of *E* and *Z* alkenes, respectively). Two extreme conformations are possible when a Ph group is attached to the point of origin of the migration. They are, according to Nickon's terminology,⁹ O-face [the face of phenyl ring projects onto an imaginary plane perpen-



dicular to the C(1)–C(2) bond axis] and O-edge (the edge of the ring projects onto this plane). The resonance interaction between Ph and the migrating C–H bond should be greatest for O-edge, whereas O-face could allow 'hominal' interaction⁹ between the π cloud and the carbene orbital and/or carbenic substituents. The fact that the amount of (*E*)-olefin (3) increased as aryl substituents in (1) (R=H) were changed from electron-withdrawing to electron-donating groups suggests that the carbene conformer *E* favours O-edge orientation (*E*-e), where H migration is affected by the electronic nature of the ring-substituents on the phenyl group at the migrating origin. For the *Z* conformer, on the other hand, O-face

[‡] Addition of the carbene to (*Z*)-4-methylpent-2-ene was stereospecific within the limits of g.l.c. detection. This is consistent with the earlier observation that the singlet chlorocarbene is involved in the cyclopropanation.

[§] It should be noted that Scheme 1 is an over-simplification and that in fact the reaction is of greater complexity than shown.

orientation (*Z*-f) would be more stable than *O*-edge orientation (*Z*-e) because the steric interaction between the phenyl and C1 group is greater in (*Z*-e) than in (*Z*-f) (Figure 1).

The relative insensitivity of (*Z*)-olefin formation to ring-substituents reflects the fact that there can be little resonance interaction between Ph and the migrating C-H bond. The attack of an alkene on the vacant p orbital of the singlet carbene conformer (*Z*-f) is thus sterically more hindered than that on the conformer (*E*-e) since the phenyl group in (*Z*-f) is parallel to the vacant p orbital which is attacked by the alkene. Thus the *E* conformer is preferentially trapped by an alkene.

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