Experimental and Theoretical Analysis of the Factors determining the Conformation and Stability of Singlet Carbene

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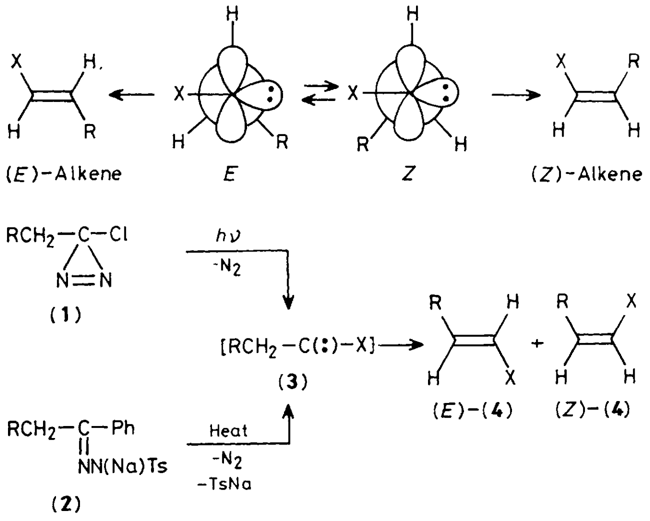
Experimental and theoretical analyses of 1,2-H shifts in singlet carbene RCH_2–C(:)–X (X = Cl, Ph) indicate that hyperconjugation of the carbene lone pair and the low-lying C–R σ^* orbital of the β-substituent plays an important role in determining the relative population of the carbene conformers.

The 1,2-H migration to divalent carbon generating an alkene is of theoretical and synthetic interest, and hence considerable efforts have been made to clarify the nature of the migration.[1,2] A topic of much recent interest is the stereochemistry of the carbene 1,2-H shift. It is generally accepted that H-migration occurs from the singlet state of the carbene. The mechanism of the 1,2-H shift involves the movement of the electrophilic hydride to the vacant p orbital of the singlet carbene, starting from approximate carbene conformers *E* or *Z* for formation of (*E*)- and (*Z*)-alkenes, respectively.[2,3] The stereochemistry of 1,2-H migration can be determined by the relative population of the conformers, which are affected by steric as well as electrostatic factors. For example, 1,2-diphenylethylidene (R = X = Ph) gave (*E*)-stilbene predominantly as a result of steric repulsion between the two phenyl rings in the conformer *Z*, while 1,2-diethoxycarbonylethylidene (R = X = CO_2Et) afforded ethyl maleate preferentially, presumably due to electrostatic repulsion between the lone pair electrons of divalent carbon and the carbonyl oxygen atom in the conformer *E*.[4] The stereochemical outcome of the migrations also affords useful information about the factors influencing the stability of singlet carbene itself. In the course of examining the effect of remote heteroatom substituents on the reactivity of carbene, we incidentally found[5] that the β-aryloxy group affects the stereochemistry of 1,2-H migration in aryloxymethylchlorocarbene in a manner which cannot be explained in terms of the steric and electrostatic effects thus far advanced. We proposed[5] that hyperconjugation of the carbene lone pair and the low-lying C–O σ^* orbital of the β-aryloxy group plays an important role in determining the relative population of the carbene conformers. To justify this assumption, we have carried out experimental and theoretical studies on the stereochemistry of 1,2-H shifts in chloro- and phenyl-carbenes bearing a series of electronegative β-substituents.

3-Chlorodiazirines (**1**) prepared by Graham's oxidation of the corresponding amidines were photolysed in 1,2-dichloroethane or cyclohexane with a 300 W high-pressure Hg lamp at 0 °C until all of the diazirine was destroyed. A Corning CS-052 filter cut-off at 350 nm was used to avoid product

Table 1. Stereoselection in 1,2-H migration to divalent carbon.

R in (3)		X = Cl (4), % (*E*)	(*Z*)	(*E*)/(*Z*)	X = Ph (4), % (*E*)	(*Z*)	(*E*)/(*Z*)
Ph	**(a)**	85.1	14.9	5.7	96.9	3.1	31.3
Me	**(b)**	67.5	32.5	2.1	80.0	20.0	4.0
Et	**(c)**	62.0	38.0	1.6	86.1	13.9	6.2
$PhCH_2$	**(d)**	27.9	58.8	0.37	85.8	14.2	6.0
$4\text{-}MeOC_6H_4CH_2$	**(e)**	31.9	68.1	0.47	—	—	—
$4\text{-}ClC_6H_4CH_2$	**(f)**	25.8	74.2	0.35	—	—	—
MeO	**(g)**	53.0	47.0	1.1	52.0	48.0	1.1
$PhCH_2O$	**(h)**	41.2	58.8	0.7	52.6	47.4	1.1
PhO	**(i)**	19.0	81.0	0.2	43.8	56.2	0.8
Cl	**(j)**	15.4	84.6	0.2	—	—	—
F	**(k)**	7.7	92.3	0.1	—	—	—



Ts = $p\text{-}MeC_6H_4SO_2$

Table 2. Relative energies (kcal mol^{-1}; 1 kcal = 4.184 kJ) of *E* and *Z* conformers of some carbenes and (*E*)/(*Z*) ratio of alkene in the 1,2-H shift.

Carbene	Energy of carbene conformer *E*	*Z*	Alkene (*E*):(*Z*)
H–C(:)–CH_2Cl	+2.13	0.00	—
Me–C(:)–CH_2OMe	+2.72	0.00	28:72[a]
Cl–C(:)–CH_2OMe	0.07	0.00	53:47[b]

[a] Ref. 7. [b] Present work.

(5) **(6)**

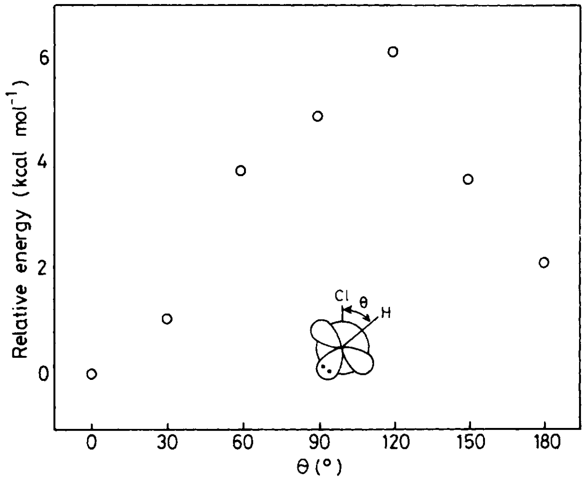


Figure 1. Total energy of :CH–CH_2Cl as a function of rotation about the C–C bond.

isomerization.† The photolysis products were almost exclusively (*E*)- and (*Z*)-chloroalkenes (**4**, X = Cl) (as evidenced by g.c.–mass spectroscopy and n.m.r. comparison with the authentic samples) which apparently arise from a 1,2-H migration in the photolytically generated chlorocarbene (**3**, X = Cl). Inspection of the results summarized in Table 1 indicates that the (*E*)/(*Z*) ratio of chloroalkenes is influenced by the β-group R; excluding R = $ArCH_2$, the amount of (*Z*)-alkene increases as more electronegative substituents are introduced on R. Similar and more ordered trends are observed in the stereochemistry of the 1,2-H shift in the corresponding phenylcarbenes (**3**, X = Ph) generated from the thermal decomposition of sodium tosylhydrazonate (**2**) (see Table 1).

These observations support the idea that hyperconjugation plays an important role in determining the relative population of the carbene conformers. Thus, since carbene has both a vacant p orbital and an occupied lone pair orbital, either orbital can be stabilized by interacting with the orbitals of the vicinal carbon. In the carbene (**3**), cationic hyperconjugation is attained when the vacant p orbital is parallel to the migrating hydrogen, which is the most positive substituent on the vicinal carbon. Anionic hyperconjugation is, on the other hand, attained by internal charge transfer between the occupied σ orbital and the unoccupied C–R σ* orbital of the vicinal bond.[6] The magnitude of this interaction, and hence the degree of stabilization, is highest when the R group is antiperiplanar to the carbenic lone pair since the σ* orbital has its greatest extension in the direction opposite to the carbenic lone pair. Obviously such interaction is attained only in the carbene conformer *Z*, while the interaction is not effective in the conformer *E*, where R is synperiplanar to the carbenic lone pair. Lone pair–polar bond hyperconjugation is described in valence bond terminology by the resonance hybrids (**5**) and (**6**); hybrid (**6**) should be more stabilized by a more

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† A control experiment indicated that the product alkenes did not isomerize under these conditions.

electronegative R group. Thus, conformer *Z* is more stabilized by negative hyperconjugation as more electronegative groups are introduced on R.

Ab initio M.O. calculations with STO-3G basis sets offer further corroborating evidence for the hyperconjugation in carbene. Figure 1 displays the total energy of $:CH–CH_2Cl$ as a function of rotation about the C–C bond. These computations revealed the *E* and *Z* conformations to represent the energy minima of the rotation surface with *Z* having the lower energy. Table 2 summarizes the relative energies calculated for *E* and *Z* conformers of the carbenes bearing a β-methoxy substituent [$X–C(:)–CH_2–OMe$]. For methylcarbene (X = Me), the *Z* conformer is calculated to be 2.72 kcal mol^{-1} more stable than the *E* conformer. This implies that the hyperconjugation is a dominant factor controlling the stability of the singlet carbene. For the corresponding chlorocarbene (X = Cl), however, the energy of the two conformers is computed to be nearly equal. This is interpreted as indicating that electrostatic repulsion between the lone pair electrons on the ether oxygen and those on the chlorine atom in the *Z* conformer becomes significant in this carbene system. It is noteworthy that the (*E*)/(*Z*) ratio of the alkene formed from these carbenes as a result of 1,2-H migration is in good agreement with that expected from the calculated stability.

The calculations were carried out on a HITAC-M200H computer, Institute for Molecular Science.

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