Origin of the Stereoselectivity of the Intramolecular 1,2-Hydrogen Shift in Singlet Chlorocarbenes. A Theoretical Study

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The stereochemistry of 1,2-H migration in ethylchlorocarbene (**1**) and chloromethylchlorocarbene (**2**) has been studied by *ab initio* methods. Geometries of the ground and transition states of a conformational equilibrium and the 1,2 rearrangement were optimized at the DFT (B3LYP) and MP2 levels of theory using 6-31G(D) and 6-311+G(D,P) basis sets. Final energies were obtained at the MP4/6-311+G(D,P)//MP2/6-311+G(D,P) level. It has been shown that the equilibrium between *cis*- and *trans*-conformers of **1** and **2** is shifted moderately toward the *trans*-conformer for carbene **1** and strongly toward the *cis*-conformer in the case of **2**. The calculated barriers of rotation about the CC bond in carbene **1** ($\Delta G^{\ddagger} = 2.3$ kcal mol^{-1}) and **2** (5.3 kcal mol^{-1}) are lower than the smallest predicted barriers of the 1,2-H shift (8.0 and 8.5 kcal mol^{-1}, respectively). In accordance with the Curtin−Hammett principle, kinetic control of stereochemistry of the rearrangement proceeding classically is realized. The predicted preferable formation of the *Z*-isomer of 1-chloropropene (**3**) and 1,2-dichloroethylene (**4**) is in good agreement with the experimental data obtained under conditions of the high-temperature thermolysis of the corresponding diazirines. Electronic factors influencing the relative stability of the *cis*- and *trans*-isomers of carbenes **1** and **2** and their transition states for 1,2-H migration are discussed.

Introduction

Investigations of the stereochemical aspect of the intramolecular 1,2-H shift in singlet carbenes[1−4] provide a clue for a more profound understanding of the mechanism of the rearrangement. Stereochemical studies of the 1,2-H migration in dialkylcarbenes have been facilitated by the possibility of using conformationally rigid bi- and tricyclic molecules.[4b−e] Such a possibility is absent for halocarbenes. In this case we have to deal with a reacting conformationally mobile system, a correct stereochemical analysis of which is possible only on the basis of the rate constant values of an equilibrium and the rearrangement of conformers. An earlier approach[2b−f] assumed *a priori* that the rotational barrier about the CC bond in halocarbenes is lower than the activation energy of the rearrangement, i.e. that the stereochemistry of the reaction is determined under kinetic control. On the other hand, the factors determining stereoselectivity of the haloalkene formation were analyzed on the basis of the conformational equilibrium of the carbenes.[2c−e]

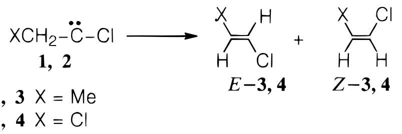
An intrinsically noncontradictory stereochemical model for understanding the origin of the stereoselectivity can be obtained by means of nonempirical quantum chemical calculations of ground and transition states of the conformational equilibrium and the 1,2-H shift in halocarbenes. Such calculations have been performed in the present work for chlorocarbenes **1** and **2** and for the products of their rearrangement, alkenes **3** and **4**. Stereoselectivity and some other aspects of the intramolecular 1,2-H shift in the chlorocarbenes have been well studied experimentally[2a,f,g,5] (Table 1). Experimental data[6,7] on the thermodynamics of alkenes **3** and **4** are available as well.

TABLE 1: Selected Literature Data on Kinetics and Stereoselectivity of the 1,2-H Shift in Carbenes 1 and 2 and on Thermodynamics of Alkenes 3 and 4

process	*T*, K	solvent		ref
1 → *Z*-**3** + *E*-**3**	295[a]	heptane	$k > 10^8$ s^{-1}	5b
	298[a]	*iso*-octane	$k \approx 10^8$ s^{-1}	5a
	343[a]	heptane	$k = 1.98 \times 10^8$ s^{-1}, $\Delta G^{\ddagger} = 7.2$ kcal mol^{-1}	5c
			$\Delta H^{\ddagger} = 4.89$ kcal mol^{-1}, $\Delta S^{\ddagger} = -8.21$ eu	5c
	373.1[b]	HMPA[c]	$Z/E = 65.6{:}34.4$	2f
	387.6[b]	cyclohexene	$Z/E = 81.7{:}18.3$	2f
	418.6[b]	gas phase	$Z/E = 78{:}22$	2g
Z-**3** ⇆ *E*-**3**	303	neat	$Z/E = 75.5{:}24.4$	6a
	423	gas phase	$Z/E = 71.6{:}28.4$	6b
2 → *Z*-**4** + *E*-**4**	298[a]		$k = 2 \times 10^7$ s^{-1}, $\Delta G^{\ddagger} = 7.5$ kcal mol^{-1}	2a
	273[a]		$Z/E = 84{:}16$	2a
	383[b]		$Z/E = 94{:}6$	2a
Z-**4** ⇆ *E*-**4**	458	gas phase	$Z/E = 63.4{:}36.6$	7a
			$\Delta H^{\circ} = 0.50$ kcal mol^{-1}, $\Delta S^{\circ} = 0.49$ eu	7a
	562	gas phase	$Z/E = 60.8{:}39.2$	7b

[a] Photolysis of the corresponding diazirine. [b] Thermolysis of the corresponding diazirine. [c] Hexamethylphosphoramide.

SCHEME 1



Computational Methods

All geometries were fully optimized at the density functional (DFT) and second-order Moller−Plesset (MP2) theoretical levels with the internal 6-31G(D) or 6-311+G(D,P) basis sets, using procedures implemented in the Gaussian 94 system of pro-

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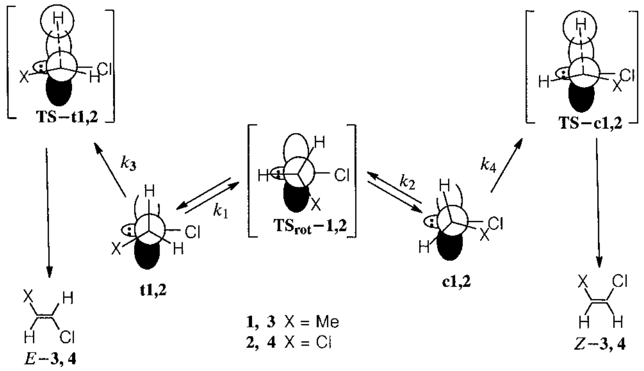
SCHEME 2



grams.[8] Single-point calculations were made at the MP4/6-311+G(D,P) level on the MP2/6-311+G(D,P) geometries. The Moller−Plesset calculations include the full core. For the DFT calculations, the “B3LYP” hybrid Hartree−Fock/DFT procedure,[9a] which uses Becke’s 88 nonlocal functional,[9b] Lee−Yang−Parr’s gradient-corrected correlation functional,[9c] and the local correlation functional of Vosko, Wilk, and Nusair,[9d] was employed. Harmonic frequency analysis verified the nature of the stationary points as minima (all real frequencies) or as transition structures (one imaginary frequency) and was used to provide an estimate of the zero-point vibration energies (ZPVE). Table S-1 of the Supporting Information shows total energies of reactants, products, and transition states along with the ZPVEs.

Heat capacities and entropy corrections were made using scaled frequencies and standard statistical procedures[10] to determine enthalpies and free energies at various temperatures. Zero-point corrections (ΔZPVE) and the frequencies were scaled by a 0.95 factor for all levels. The derived entropy, enthalpy, and free energy changes of the species for the conformational equilibrium and 1,2-H shift in carbenes **1** and **2** at 298 K are given in Table S-2 of the Supporting Information.

Molecular orbitals of **1**−**4** are displayed as modified Jorgensen−Salem plots.[11]

Selected structural data are given in Tables S-3 and S-4 of the Supporting Information.

Results and Discussion

The calculations at all levels of theory have shown that singlet ethylchlorocarbene (**1**) exists in the form of two conformers **c1** and **t1** with *cis* and *trans* orientation of the methyl group and chlorine atom, respectively, with **t1** somewhat more stable than **c1**. Both conformers belong to the C_1 point group of symmetry; the out-of-plane C−C−C−Cl torsion angles are 12.6° and 15.5°, respectively. The C_s structures of **c1** and **t1** were also considered. It was found that at the B3LYP and MP2/6-31G(D) levels rotamer **c1**-C_s is also a minimum and has practically the same total energy as **c1**−C_1. However, the MP2 method using the more expanded basis set, 6-311+G(D,P), indicates that the C_s structure of **c1** is a saddle point (one imaginary frequency) on the vibrationless Born−Oppenheimer surface, although the zero-point correction makes this structure 0.1 kcal mol^{-1} more stable than **c1**-C_1. On the other hand, structure **t1**-C_s was found at all theoretical levels as the transition state of the rotation about the CC bond connecting the enantiomeric forms of **t1**-C_1, although the destabilization of **t1**-C_s relative to **t1**-C_1 is very small, $<$0.35 kcal mol^{-1}.

The interconversion of the diastereomeric conformers **c1** and **t1** proceeds through the transition state **TS$_{rot}$-1** (Scheme 2).

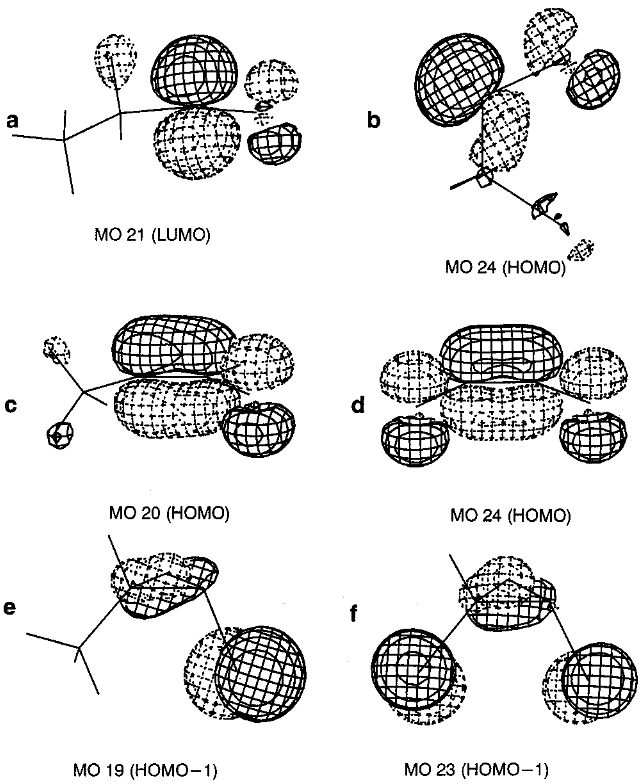
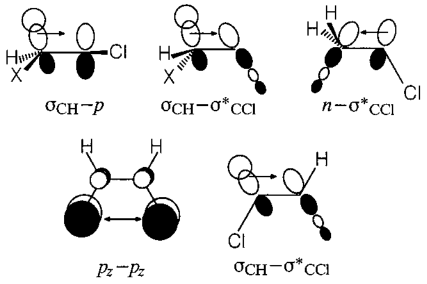


Figure 1. Lowest unoccupied molecular orbital of the *trans*-conformer **t1** (a) and the highest occupied molecular orbitals of the *cis*-conformer **c2** (b), alkenes *Z*-**3** (c) and *Z*-**4** (d), and the second highest molecular orbitals of the *cis*-transition states **TS-c1** (e) and **TS-c2** (f).

SCHEME 3



The tendency of the two rotamers to adopt twisted rather than planar forms may be understood in terms of the interaction of the adjacent group orbitals, specifically a stabilizing two-electron interaction between the vacant carbene 2p orbital and the occupied σ orbital of a C−H bond of the methylene group (Scheme 3). This type of interaction is present in all singlet carbenes and ultimately leads to the 1,2-H (or 1,2-alkyl) migration to form the product alkene. In the twisted conformation, one such C−H bond can adopt a quasi-parallel orientation relative to the empty 2p orbital at the carbene site. This interaction is readily apparent in the lowest unoccupied molecular orbital (LUMO) shown for **t1** in Figure 1a.[12] The elongation of the donor C−H bond (1.11 Å) and the decrease of the H−C−C valence angle (98.8°) are geometrical consequences of the σ_{CH}-p orbital interaction. The interaction, which is analogous to hyperconjugation in carbocations, is more important for C−H bonds than for C−C bonds, hence the geometry of **TS$_{rot}$-1** (Scheme 2).

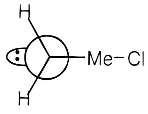
Destabilization of the *cis*-conformer **c1** in comparison with **t1** {e.g. the *trans*-rotamer **t1**-C_s is 0.33 kcal mol^{-1} [MP4/6-311+G(D,P)//MP2/6-311+G(D,P) + ΔZPVE] more stable than the *cis* **c1**-C_s} might be expected on the basis of steric repulsion of the methyl group and chlorine atom, but this explanation

TABLE 2: Calculated Equilibruim[a] *Z/E* Ratios of Alkenes 3 and 4 and Predicted Stereoselectivities of Their Formations in the 1,2-H Rearrangement of Carbenes 1 and 2 at Various Temperatures

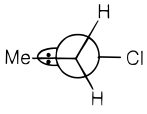
		6-31G(D)		6-311+G(DIP)	
	T, K	B3LYP	MP2	MP2	MP4SDTQ
		1-Chloropropene (**3**)			
alkene equilibrium					
Z-**3** $\rightleftharpoons$ *E*-**3**	298	61.6:38.4	64.9:35.1	73.0:27.0	70.1:29.9
	303	61.5:38.5	64.8:35.2	72.8:27.2	70.0:30.0
	423	60.1:39.9	63.2:36.8	70.0:30.0	67.9:32.1
carbene equilibrium					
c1 $\rightleftharpoons$ **t1**	298	8.7:91.3	45.6:54.4	30.9:69.1	29.1:70.9
	418.6	16.6:83.4	49.4:50.6	36.8:63.2	35.4:64.6
Curtin−Hammett control					
Ts-c1, **TS-t1**	298	81.0:19.0	76.5:23.5	71.6:28.4	74.6:25.4
	418.6	76.8:23.2	73.8:26.2	70.6:29.4	72.8:27.2
		1,2-dichloroethylene (**4**)			
alkene equilibrium					
Z-**4** $\rightleftharpoons$ *E*-**4**	298	50.2:49.8	65.1:34.9	68.9:31.1	63.3:36.7
	458	48.9:51.2	58.9:41.1	61.6:38.4	57.7:42.3
	562	48.3:51.7	56.6:43.7	58.9:41.1	55.6:44.4
carbene equilibrium					
c2 $\rightleftharpoons$ **t2**	298	99.6:0.4	98.4:1.6	98.1:1.9	96.4:3.6
	383	98.4:1.6	95.2:4.8	95.1:4.9	92.2:7.8
Curtin−Hammett control					
TS-c2, **TS-t2**	298	100:0	100:0	99.98:0.02	99.98:0.02
	383	99:98:0.02	99.96:0.04	99.9:0.1	99.9:0.1

[a] Based on thermodynamic data listed in Table S-2.

may be too simplistic in view of the fact that the *cis*-isomer of the product alkene *Z*-**3** is more stable than the *trans*-isomer *E*-**3**.



c1−C_s



t1−C_s

The profile of the potential energy of rotation about the C−C bond in singlet chloromethylchlorocarbene (**2**) is qualitatively similar to that of **1**: local minima corresponding to *cis*- and *trans*-conformers **c2** and **t2**. At all levels of theory, the nonplanar rotamer, *cis*-rotamer **c2**-C_1, and the planar, **c2**-C_s, are both minima and have virtually the same energy. The *trans*-rotamer **t2** has C_1 symmetry on the vibrationless Born−Oppenheimer surface, while the planar structure **t2**-C_s is a transition state. However, unlike the case of **t1**, the "saddle point" **t2** lies 0.11 kcal mol^{-1} lower than **t2**-C_1 after inclusion of ZPVE. On the whole, it can be concluded that the *cis* and *trans* ground states of carbene **2** as well as **1** oscillate around the corresponding C_s structures without any barrier.

Besides the σ_{CH}−p interaction discussed in the case of **1**, the presence of the second chlorine in place of the methyl group in chloromethylchlorocarbene (**2**) introduces a new factor that will affect the relative energy of the *cis,trans*-rotamers: the attractive two-electron interaction of the nonbonding (n) carbene sp^2 orbital with the antibonding σ^* orbital of the vicinal C−Cl bond (Scheme 3). The interaction manifests itself as a weak involvement of C−Cl σ^* in the highest occupied molecular orbital (HOMO) of **c2**-C_s (Figure 1b). The influence of this kind of interaction on the conformational equilibrium of carbenes has been discussed on a qualitative level[2d] and has been the objective of previous *ab initio* calculations (HF/STO-3G).[2c] The n−σ^*_{CCl} interaction is strongest in **c2**, which has an anti-periplanar arrangement of the n and σ^* orbitals. It is confirmed by the significant lengthening of the C−Cl bond (1.787 Å vs 1.769 Å in **t2**) and shortening of the C−C bond (1.477 Å vs 1.493 Å in **t2**) in this rotamer in comparison with **t2** (and **TS$_{rot}$-2** (Table S-4)), which has a less favorable orientation of these orbitals. As a consequence, unlike ethylchlorocarbene (**1**), the *cis*,*trans*-equilibrium of chloromethylchlorocarbene (**2**) is considerably shifted toward the *cis*-rotamer **c2**. Therefore the n−σ^*_{CCl} interaction is the more important factor in comparison with the σ_{CH}−p interaction. A decrease of both stabilizing interactions in the transition state **TS$_{rot}$-2** leads to the fairly significant barrier of the nondegenerate rotation about the C−C bond in carbene **2** (5.3 kcal mol^{-1}, Table S-2).

The calculations of the transition states of the hydrogen 1,2 shift in both carbenes **1** and **2** at all levels of theory predict that the energies of the *cis*-transition stuctures, **TS-c1** and **TS-c2**, are lower than of the *trans* ones, **TS-t1** and **TS-t2**, 8.0 and 8.5 compared to 8.7 and 13.7, respectively ($\Delta G^{\ddagger}$ in kcal mol^{-1}, Table S-2). According to our data (Tables S-3, S-4) and earlier calculated data of Evanseck and Houk,[13a] the geometry of the transition state of the rearrangement is closer to the product, an alkene, than to the initial carbene. Hence one can suppose that factors that govern the equilibrium *Z*/*E* ratio in alkenes **3** and **4** will also influence the relative energies of *cis*- and *trans*-**TS-1,2**.

The experimental (Table 1) and calculated data (Tables 2, S-1, S-2) indicate the greater stability of the *Z*-isomer of alkenes **3** and **4**. The predicted equilibrium *Z*/*E* ratios that are closest to the experimental ones were obtained at the MP2/6-311+G-(D,P) level. The stabilization of the *Z*-isomers **3** and **4** has been attributed to the through-space interaction of the p_z orbitals localized on the terminal atoms.[14] These orbitals are in phase in the HOMOs of the *Z*-alkenes **3** and **4** (Figure 1c,d, Scheme 3) and are the p_z-like group orbital of the methyl group and the nonbonding 3p_z orbital of the chlorine atom in *Z*-**3** and the nonbonding 3p_z orbitals of the two chlorine atoms in *Z*-**4**. An additional factor must be the donor−acceptor interaction between the C−H bond (σ_{CH}) and the anti-periplanar C−Cl bond (σ^*_{CCl}) (Scheme 3). The principal differentiating factor between **3** and **4** is the electrostatic interaction of the bond dipoles. The attractive dipole−dipole interaction of the C−Cl and C−C_{Me} bonds in *Z*-**3** also promotes stabilization of this isomer, whereas *Z*-**4** has to be destabilized to some degree by the repulsive dipole−dipole interaction of the two C−Cl bonds. As a result the *Z*/*E* ratio is markedly greater for chloropropene **3** than it is for dichloroethylene **4** (Tables 1, 2).

The stabilizing "p_z-p_z" and $\sigma_{CH} - \sigma^*_{CCl}$ interactions (Scheme 3) are operative in the transition states **TS-c1** and **TS-c2** of the 1,2-H shift, as is evident from the shorter C−C bonds (Tables S-4, S-5) and by shorter distances between the terminal atoms in comparison with the initial carbenes **c1** and **c2**. As well as by these interactions, **TS-c2** is additionally stabilized by the previously mentioned $n-\sigma^*_{CCl}$ hyperconjugation, which contributes to an increase in the difference in energies of this isomer and **TS-t2** compared to the difference between **TS-c1** and **TS-t1** (5.2 kcal mol^{-1} compared to 0.6 kcal mol^{-1}). In each case, the *cis*-TS, which will form the *Z*-alkene, is more stable than the *trans*-TS, which will lead to the *E*-alkene.

The predicted enthalpies of activation and, correspondingly, free energies of activation of the 1,2-H migration in chlorocarbenes **1** and **2** depend somewhat on the computational method (Table S-2). The MP2 method with either basis set gives $\Delta G^{\ddagger}$ values for the *cis*-conformer **c2** that are closest to the experimental value[2a] (Table 1). There are only approximate experimental estimates[5] of the rate constant of the rearrangement of carbene **1**. A value of $\Delta G^{\ddagger} < 6.5$ kcal mol^{-1} can be assumed from these estimates. The calculated $\Delta G^{\ddagger}$ values obtained by the MP2/6-311+G(D,P) method for both rotamers **c1** and **t1** do not exceed this assumed value.

The calculated entropies of activation of the 1,2-H migration in chlorocarbenes **1** and **2** depend somewhat on the computational method (Table S-2). They are similar to an earlier calculated value (−3.1 eu) for methylchlorocarbene.[13] Experimental values of $\Delta S^{\ddagger}$ of the rearrangement of both carbene **1** (−8.21 eu)[5c] and methylchlorocarbene (−14.2 eu)[5b] are more negative than the values calculated for **1** and **2**. The rearrangement of another chlorocarbene, benzylchlorocarbene, is also characterized by a significant negative entropy of activation (−7.7 eu).[15] An experimental value of $\Delta S^{\ddagger}$ for the chlorocarbene **2** has not been measured.[2a,16a] Large negative entropies of activation of the 1,2 rearrangement of carbenes are usually connected with quantum mechanical hydrogen tunneling,[13b,16] which begins to dominate at temperatures below 300 K. Location of the transition states by means of the computational methods used in the present work supposes a classical mechanism of the reaction. Such a mechanism is realized at higher temperatures.[16] Presumably the 1,2-H shift in the chlorocarbenes **1** and **2** generated under conditions of thermolysis of the corresponding diazirines, i.e. at 377−383 K (Table 1), proceeds mainly classically.

At the temperatures of the thermolysis, the alkene products do not isomerize, and so the relative abundances of the *Z*- and *E*-diastereomers reflect the relative rates of their formation; that is, the reaction (Scheme 2) proceeds under kinetic control. The calculated values of free energies of activation of the 1,2-H migration in carbenes **1** and **2** are markedly higher than the barriers of rotation about the C−C bond in these compounds (Table S-2), especially in the case of **1**. Under such circumstances, the Curtin−Hammett principle[17] should apply, and the observed *Z*/*E* ratio of product alkenes should provide no information about the relative stabilities of the precursor diastereomeric carbenes. However, Zefirov[18] has demonstrated that intermediate cases may apply in which the relative thermodynamic stability of the reactants can influence the product distribution. In the case of ethylchlorocarbene (**1**), the Curtin−Hammett limit seems to be confirmed by comparison of the experimental and theoretical *Z*/*E* stereoselectivities. Indeed the ratio of the *Z*,*E*-isomers of chloropropene **3** predicted on the basis of the equilibrium ratio of *cis*,*trans*-conformers **c1** and **t1** (Table 2) is opposite the experimentally observed *Z*/*E* ratio (Table 1), whereas the calculation of the stereoselectivity on the basis of the difference of free energies of transition states **TS-c1** and **TS-t1** gives fairly satisfactory agreement with observation. In addition, the computations at all levels predict greater polarity of the *trans*-transition state **TS-t1** in comparison with the *cis* one **TS-c1** (Table S-3). Therefore one can expect a decrease of *Z*-stereoselectivity of the kinetically controlled rearrangement of carbene **1** in polar solvents owing to a greater stabilization of the more highly solvated species **TS-t1**. Such a decrease of the stereoselectivity in polar solvents has been experimentally observed[2f] (Table 1). In contrast to this, *cis*-conformer **c1** has a greater dipole moment than **t1** (Table 2), and in the intermediate case where the thermochemistry of the carbene precursors may play a role, one might observe an increase of *Z*-stereoselectivity in polar media.

For chloromethylchlorocarbene (**2**), the strong preference of the *cis*-isomer in both the ground state and the 1,2-H migration transition state inevitably leads to *Z*-stereospecificity. However, the observed diastereoselectivity of dichloroethene formation is not nearly as high as would be predicted from the relative energies of **TS-c2** and **TS-t2** (Tables 1, 2). Since the difference between energies of **TS-c2** and **TS$_{\mathbf{rot}}$-2** is not as large as the corresponding difference in **1**, one may enquire whether the discrepancy may be due to the reaction kinetics operating in the "intermediate region" where the carbene equilibrium plays a role in determining the stereochemical outcome of the alkene formation.

The general equation[18] of the relationship between the stereoselectivity and rate constants of a reacting conformationally mobile system such as the present case (Scheme 2) is

$$(Z/E) = K_{eq}k_4(k_1 + k_2 + {}_{k3})/k_3(k_1 + k_2 + k_4)$$

where $K_{eq} = k_1/k_2$, k_1, k_2 are the rate constants of the conformational equilibrium (Scheme 2), and k_3, k_4 are the rate constants of the 1,2-H shift (Scheme 2).

Relative values of the rate constants may be derived directly from differences between the predicted free energies (Table S-2). From the predicted values of the differences in the conformational energies of the carbenes ($\Delta G°$) and free energies of activation of the 1,2-H shift ($\Delta\Delta G^{\ddagger} = \Delta G_3^{\ddagger} - \Delta G_4^{\ddagger}$), one can estimate a range of $\Delta G^{\ddagger}$ values for the reaction proceeding from the limiting Curtin−Hammett case[17] to an intermediate region and possibly further to where the relative abundances of the carbenes control product alkene distribution. In Figure 2 is shown the variation of the product diastereoselectivity (log(*Z*/*E*)) as a function of the barrier height to the formation of the *Z*-alkene, $\Delta G_4^{\ddagger}$. The rate constants were calculated from the ΔG values obtained by the MP4/6-311+G(D,P)//MP2/6-311+G(D,P) method (Table S-2), assuming that the relative energies of the *cis*- and *trans*-carbenes and the connecting transition structure, **TS$_{\mathbf{rot}}$**, as well as the difference between the 1,2-H transition structures, $\Delta\Delta G^{\ddagger}$, were correctly predicted (the theoretically predicted 298 K values (Table S-2) were used). Thus, variation of $\Delta G_4^{\ddagger}$ is equivalent to varying the relative magnitudes of the barriers to rotation and 1,2-H rearrangement.[19] The upper flat portions of the curves in Figure 2 represent the regions where the Curtin−Hammett principle applies. Curvature in the curve represents the intermediate region which begins at $\Delta G_4^{\ddagger} = 3.5$ kcal mol^{-1} in the case of carbene **1**, i.e. when the lower barrier to 1,2-H migration is approximately 2 kcal mol^{-1} higher than the rotational barrier. In the case of carbene **2**, the intermediate region begins at $\Delta G_4^{\ddagger} = 5$ kcal mol^{-1}, approximately at the point when the lower barrier to 1,2-H

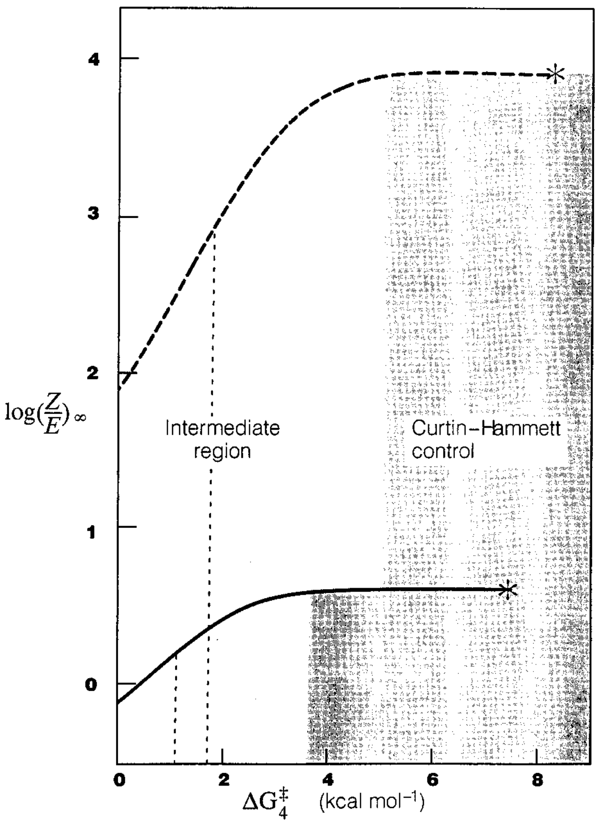


Figure 2. Logarithmic dependences of the *Z*/*E*-stereoselectivity on the free energy of activation ($\Delta G_4^\ddagger$), the *cis*-carbene → *Z*-alkene process, see Scheme 2) of the 1,2-H shift in carbenes **1** (—, $\Delta G° = 0.53$ kcal mol^{-1}, $\Delta\Delta G^\ddagger = 1.17$ kcal mol^{-1}) and **2** (- - -, $\Delta G° = 1.96$ kcal mol^{-1}, $\Delta\Delta G^\ddagger = 3.22$ kcal mol^{-1}). The points corresponding to the calculated values (MP4/6-311+G(D,P)//MP2/6-311+G(D,P)) of log (*Z*/*E*) and $\Delta G_4^\ddagger$ are marked by the asterisks.

migration and the rotational barrier are the same magnitude. The computed free energy parameters predict quite well the product diastereoselectivity in the case of **3** but do not account for the larger than expected amount of the *E*-isomer of **4**.

Concluding Remarks

The equilibrium between the *cis*- and *trans*-conformers of ethylchlorocarbene (**1**) and chloromethylchlorocarbene (**2**) is mainly controlled by orbital interactions: by the σ_{CH}–p interaction, which stabilizes principally the *trans*-conformer **t1** in the first case, and by the n–σ_{CCl}^* interaction, strongly stabilizing the *cis*-conformer **c2** in the second case.

The reaction in carbenes **1** and **2** is modeled computationally as following a classical pathway (as opposed to one with substantial quantum mechanical tunneling) for the intramolecular 1,2-H shift. This is a realistic approximation under the conditions of the high-temperature thermolysis of the corresponding diazirines.[2a,f,g] According to the calculations, the barriers of rotation about the CC bond in carbenes **1** and **2** are lower than the barriers of the 1,2-H migration. Therefore in accordance with the Curtin–Hammett principle,[17,18] the *Z*/*E*-stereoselectivity must be determined by the difference in energies of the *cis*- and *trans*-isomeric transition states. The smaller energy of the *cis*-transition state, which affords the *Z*-isomer of alkenes **3** and **4** is attributed to a stabilizing through-space p_z–p_z orbital interaction of the terminal atoms and σ_{CH}–σ_{CCl}^* interactions involving the polar C–Cl bonds.

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Supporting Information Available: Tables S-1 to S-4 showing total energies of the reactants and products; entropy, enthalpy, and free energy changes of the equilibrium species; and selected structural data (4 pages). Ordering information is given on any current masthead page.

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