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Influence of Bystander Substituents on the Rates of 1,2-H and 1,2-Ph Shifts in Singlet and Triplet Carbenes

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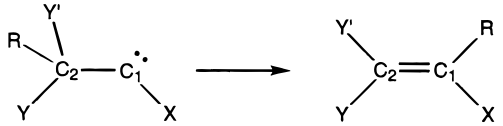
Substituent effects at the migration origin on the rate of rearrangement of several alkylchlorocarbenes have been studied at the B3LYP/6-311G**//B3LYP/6-31G* level. Methyl, halo, and phenyl groups are found to accelerate 1,2-H shift rearrangements in the order Ph > Me > F > Cl > H. Methyl groups are also found to accelerate both singlet and triplet 1,2-Ph shifts in benzylchloro- and benzylcarbenes. A direct comparison of the 1,2-H shift in methylchlorocarbene and the 1,2-Ph shift in benzylchlorocarbene shows that the inherent migratory preference of a phenyl group is greater than that of a hydrogen atom. Significant bystander substituent effects are found, as originally proposed by Nickon.

Introduction

Many experimental studies have illustrated the strong influence of substituents on carbene rearrangement rates. Substituent effects at the carbene center are dramatic: while methylcarbene reacts by 1,2-H shift too quickly to be detected experimentally,[1] methylchlorocarbene (**1**) has a lifetime of 300−700 nanoseconds.[2,3] Computed activation energies for these rearrangements at the MP2 level suggest $\Delta E_a = 10.9$ kcal/mol.[4] Carbene 1,2-H shift rearrangements are also known to be sensitive to substitution at the migration origin, labeled C_2 in Scheme 1.[3,5] Recent experimental studies reveal that these rates also span a significant range, with carbene lifetimes ranging from two to hundreds of nanoseconds depending on the bystander group Y.[6]

The structure of organic carbenes is responsible for their large sensitivity to substituent effects at the C_1 center. Electron donors at this position stabilize the empty p orbital of lowest $^1A_1$ singlet carbenes and make them less reactive. Evanseck and Houk have reported an excellent correlation between the activation energies of substituted carbene rearrangements and the σ_R values of various C_1 substituents including hydroxy, methoxy, chlorine, fluorine, and vinyl groups.[4]

SCHEME 1



The structure of the 1,2-R shift transition state is responsible for the effects of substituents at the C_2 center. Carbene 1,2-H shift transition structures, for example, largely resemble the planar alkene products, except for the migrating hydrogen that bridges the C_1 and C_2 carbons. The transition state is very late in terms of the alkene planarization, but it is early in terms of the position of the migrating H relative to its position in the product, as determined by a number of computational studies.[4,7−10] Of importance to the role of substituents, the 1,2-H shift in singlet carbenes occurs with significant charge separation; negative charge decreases at C_2 and increases at C_1 in the transition state.[11] The early stages of a 1,2-H shift can be thought of as resembling a hydride shift, in which electron density moves from C_2 to C_1 in the π-system without the involvement of the carbene lone pair. Experimental evidence for charge separation in 1,2-H shifts has been seen in the acceleration of the rearrangements of 1-phenylethylidene and dimethylcarbene in polar solvents such as acetonitrile.[5,12] This feature of the reaction suggests that substitution of electron-donating groups at C_2 should lead to rate acceleration by stabilizing the electron-deficient C_2 center in the transition state relative to the carbene. This idea is the basis for the study described here.

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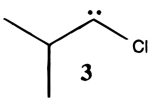

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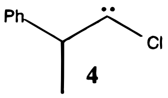

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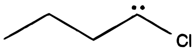

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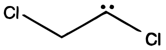

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The acceleration of 1,2-H shifts by alkyl bystander substituents has been quantified experimentally by a number of groups. In 1989 LaVilla and Goodman reported the absolute rates of rearrangement of methyl (**1**), ethyl (**2**), and isopropylchlorocarbene (**3**) as determined by photoacoustic calorimetry. They found that the 740 ns lifetime of methylchlorocarbene was reduced to less than 10 ns (the time resolution of their experiment) by the addition of one or more methyl C_2 substituents.[3] Liu and Bonneau recently repeated similar measurements with improved time resolution and assigned lifetimes of 2, 17, 18, and 330 ns to α-methylbenzylchlorocarbene (**4**), *n*-propylchlorocarbene (**5**), benzylchlorocarbene (**6**) and methylchlorocarbene (**1**), respectively. In a study of dialkylcarbenes, Modarelli et al. found that an ethyl bystander reduces the lifetime of dimethylcarbene in pentane from 21 to 2 ns.[12] Sugiyama et al. have also reported that the 1,2-H shift of 1-phenylethylidene is accelerated by more than a factor of 60 when a methyl group is added at C_2 to give 1-phenylpropylidene.[5] Experimentally determined lifetimes for carbene rearrangements that illustrate the effect of substituents at C_2 are reported in Table 1.

TABLE 1: Lifetimes for Carbenes 1−7 (Limited by Rates of 1,2-H Shift)

compd	exptl lifetime (ns) at 298 K	ref
1	∼330	2
	∼700	3
2	<10	3, 13
3	∼10	6
4	2	6
5	2	6
6	16	14
7	50	15

TABLE 2: Bystander Assistance Factors for Hydrogen Migration in Dialkyl Carbenes[22]

Y	*B*[Y]	*B*[Y^{anti}]	*B*[Y^{syn}]
Ph	9.2	7.4	1.8
Me	28.5	20.1	8.4
Et	32.3	26.6	5.7
allyl	28.1	22.6	5.5
MeO	73.5	20.3	53.3

The only rearrangement products observed from **4** and **6** result from 1,2-H shifts, despite the theoretical possibility of competitive singlet-state 1,2-Ph migration. This is consistent with the generally accepted rate of migratory aptitude H > Ph > Me, which has been reported from competition studies.[16−18] In 1993 Nickon proposed the unconventional view that intrinsic migratory aptitudes for different R groups may be misleading when analyzing carbene rearrangement preferences. He suggested that product ratios are instead frequently determined by the relative abilities of different bystander groups at C_2 to accelerate the reaction. Experimental studies and a survey of the literature led him to tabulate “bystander assistance factors”, *B*[Y], for a number of functional groups. These are shown in Table 2 and represent the factor by which the group Y will accelerate the 1,2-H shift rearrangement of dialkyl carbenes, relative to hydrogen. The *B*[Y] values depend on the position of the Y group, syn or anti, relative to the carbene C_1 substituent. Nickon concluded, on the basis of these data and competition experiments using isotopically labeled benzylcarbene, that the intrinsic migratory aptitude of a phenyl group is actually larger than that of a hydrogen atom.[19]

A significant complication in Nickon’s analysis is that dialkyl and benzyl carbenes have triplet ground states.[20] This is particularly significant where competitive product yields were used to infer the relative migratory aptitudes of H and Ph groups. Since it is commonly believed that 1,2-Ph but not 1,2-H shifts can occur in the triplet state, it is likely that Nickon was measuring a complicated interplay of spin-state equilibrium and rearrangement rates.[32b] Nickon’s results may also be questioned in light of the possible role of precursor reactivity, now known to be important in many “carbene” rearrangements.[12] His analysis of results based on the thermolysis of tosylhydrazone salts does not account for the possible rearrangement of the precursor under the reaction conditions.[21] Despite possible weaknesses of Nickon’s hypothesis, we found the suggestion that bystander effects may mask the true migratory preferences of different groups intriguing.

Computational Methodology

Calculations were performed with Gaussian 94.[23] Stationary points were fully optimized and characterized by the number of imaginary frequencies. Zero-point energy (ZPE) corrections were made with a frequency scaling factor of 0.9806[24] and are included in reported activation energies and other energy differences unless otherwise noted. The calculation of entropies and free energies also used a frequency scaling factor of 0.9806; these were carried out for standard temperature and pressure.

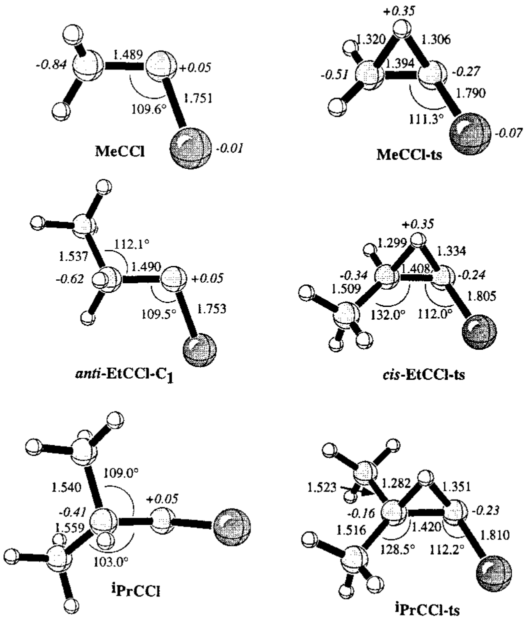


Figure 1. B3LYP/6-31G* geometries for lowest-energy carbene conformers and 1,2-H shift transition states for the rearrangements of methylchlorocarbene, ethylchlorocarbene, and isopropylchlorocarbene.

Geometries were optimized using the hybrid Hartree−Fock/density functional methods Becke3LYP (B3LYP) and unrestricted Becke3LYP (UB3LYP)[25−27] with the 6-31G* basis set. Electron correlation has been shown to have a strong influence on carbene transition-state geometries.[4] Given the large size of some of the carbenes considered, density functional theory is appropriate because it is very time efficient compared to MP2 and higher order perturbative methods. The Cramer and Schaefer groups have also reported successful application of density functional methods to the study of carbene rearrangements and singlet−triplet gaps.[28−30]

B3LYP/6-31G* activation energies (E_a’s) give good agreement with much more intensive theoretical methods for the 1,2-H shift in **1**.[31] Single-point energy corrections at the B3LYP/6-311G** level are also reported here, however, and these give better agreement than the B3LYP/6-31G* results with CBS-Q calculations on the rearrangement of 1,2-dichloroethylidene.[32]

All barriers reported assume Curtin−Hammett kinetics and are given as the energy difference between the transition state and the lowest energy conformer of the carbene. We have verified that the barriers to isomerization of carbene conformers are lower than the barriers to rearrangement for isopropylchlorocarbene and 1,2-dichloroethylidene. Shustov et al. report that ethylchlorocarbene follows this paradigm as well.[33]

Atomic partial charges were computed using the natural population analysis (NPA) method of Reed and Weinhold.[34−36] Electron densities for the evaluation of NPA charges were computed at the MP2/6-31G* level, using B3LYP/6-31G*-optimized geometries.[37]

Results

Alkylchlorocarbenes. The lowest energy conformers of methylchlorocarbene (MeCCl), ethylchlorocarbene (EtCCl), and isopropylchlorocarbene (^{i}PrCCl) are shown in Figure 1. The NPA partial charges on the carbene carbons are similar in all

TABLE 3: B3LYP/6-31G* Barriers to 1,2-H and 1,2-Ph Shifts in Methylchlorocarbene, Ethylchlorocarbene, and Isopropylchlorocarbene in kcal/mol[a]

rearrangement	stationary points for E difference	E_a	E_a with ZPE	$\Delta G^‡$	$\Delta S^‡$ (e.u.)
methylchlorocarbene 1,2-H shift	MeCCl	15.1	13.5	14.2	−3.8
	MeCCl-ts	(13.1)	(11.5)	(12.2)	
cis-ethylchlorocarbene 1,2-H shift	*cis*-EtCCl-ts	10.1	8.2	8.4	−1.6
	anti-EtCCl	(8.7)	(6.8)	(7.0)	
trans-ethylchlorocarbene 1,2-H shift	*trans*-EtCCl-ts	10.7	8.8	9.3	−2.7
	anti-EtCCl	(9.0)	(7.0)	(7.6)	
isopropylchlorocarbene 1,2-H shift t.s.	^{i}PrCCl-ts	7.7	5.3	5.8	−2.3
	$^{\mathrm{i}}$PrCCl-A	(6.3)	(3.9)	(4.4)	
isopropylchlorocarbene 1,2-H shift t.s.	^{i}PrCCl-ts	^{i}6.3	4.3	4.9	−2.4
	$^{\mathrm{i}}$PrCCl-B	(4.9)	(2.9)	(3.4)	

[a] B3LYP/6-311G**//B3LYP/6-31G* energies in parentheses. $\Delta G^‡$ and $\Delta S^‡$ at 298 K.

cases (+0.05). Transition structures for the 1,2-H shifts in these carbenes also shown in Figure 1 and are referred to as MeCCl-ts, *cis*-EtCCl-ts, and $^{\mathrm{i}}$PrCCl-ts. Alkyl substitution at C_2 gives rise to earlier transition states, with the breaking C−H bond length decreasing from 1.320 Å in MeCCl-ts to 1.312 Å in *trans*-EtCCl-ts, 1.299 Å in *cis*-EtCCl-ts, and 1.282 Å for $^{\mathrm{i}}$PrCCl-ts. The migration of electron density from C_2 to C_1 is apparent in these transition states, with a partial negative charge developing at the carbene center and negative charge decreasing at C_2. The change in dipole moment between the carbene and the transition state due to this polarization is +1.26, +1.69, +1.47, and +1.69 D for the methyl, *trans*-ethyl, *cis*-ethyl-, and isopropylchlorocarbene 1,2-H shifts; the changes in charge at C_2 are +0.33, +0.32, +0.28, and +0.25 for these rearrangements.

The influence of alkyl substitution on the reaction energetics is shown in Table 3. Activation energies for MeCCl, *trans*-EtCCl, *cis*-EtCCl, and $^{\mathrm{i}}$PrCCl are 11.5, 7.0, 6.8, and 3.9 kcal/mol at the B3LYP/6-311G** level. Addition of one methyl group to methylchlorocarbene lowers the activation energy by 4.5−4.7 kcal/mol, while addition of two methyl groups leads to a decrease of 7.6 kcal/mol. The free energy changes involved are 4.6−5.2 and 7.8 kcal/mol, giving a free energy of activation of only 4.4 kcal/mol for the 1,2-H shift in $^{\mathrm{i}}$PrCCl, compared to 12.2 kcal/mol for MeCCl.

Halo-substituted Alkylchlorocarbenes. We have previously reported structures and energies for the 1,2-H shift in 1,2-dichloroethylidene ($ClCH_2CCl$) at the MP2/6-31G† and CBS-Q levels.[32] Structures of stationary points at the B3LYP/6-31G* level are shown in Figure 2 along with fluoromethylchlorocarbene (FCH_2CCl) and its 1,2-H shift transition structure. Stabilization of the transition state by chlorine or fluorine at C_2 in this case is effected by hyperconjugative interactions between the carbene lone pair and the low-lying C−Cl or C−F σ^* orbitals, which also lead to a strong preference for formation of the *Z* product.[32] The shortening of the C_1−C_2 bond and lengthening of the C_2−Cl bond seen in $ClCH_2CCl$ are also apparent in FCH_2CCl but, to a lesser extent, consistent with the higher energy of a C−F σ^* compared to a C−Cl σ^* orbital.

Hyperconjugative interactions involving C_2 substituents occur only in the cis conformation; by examining trans conformers we can analyze the substituent effect of a halogen without its dominant hyperconjugative element. Energies for the 1,2-H shifts in *trans*-$ClCH_2CCl$ and *trans*-FCH_2CCl are reported in Table 4. These show that *trans*-chloro substitution reduces the 1,2-H shift barrier by only 0.6 kcal/mol from that in methylchlorocarbene; *trans*-fluoro substitution reduces the barrier by 2.5 kcal/mol. The breaking C_2−H bond lengths are 1.306 and 1.294 Å, respectively, for *trans*-$ClCH_2CCl$-ts and *trans*-FCH_2CCl-ts; these are close to the value in EtCCl.

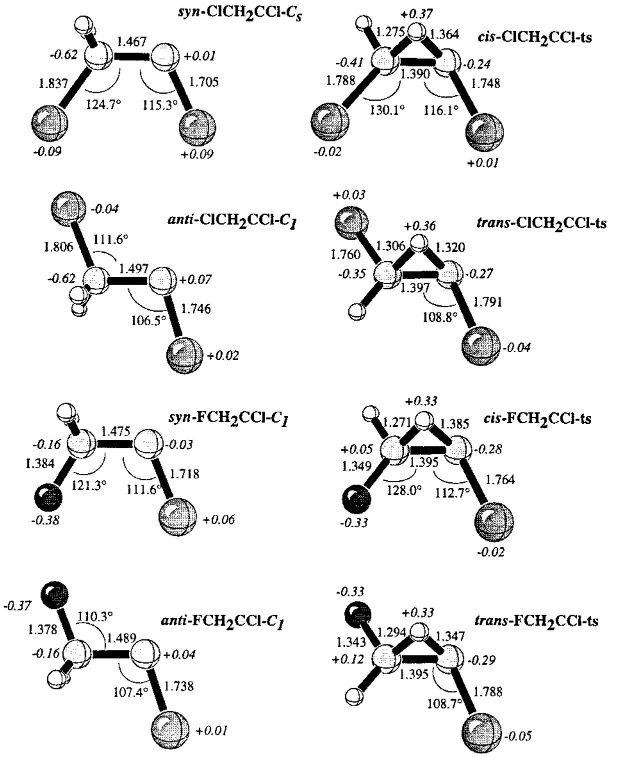


Figure 2. B3LYP/6-31G* geometries for lowest-energy carbene conformers and 1,2-H shift transition states for the rearrangements of 1,2-dichloroethylidene and 1-chloro, 2-fluoroethylidene.

Benzylchlorocarbene. The minimum electronic energy conformer for benzylchlorocarbene (BnCCl−B) has the phenyl group face-on to the empty carbene p-orbital, as shown in Figure 3. Inclusion of zero-point energy favors a conformation with the phenyl and chloro groups anti, with one of the hydrogens aligned with the empty p-orbital (BnCCl-A). A third conformer (not shown) has the chlorine and the phenyl groups syn and is higher in energy by 0.7 kcal/mol at the B3LYP/6-31G* level.

In the transition state for the trans-1,2-H shift (*trans*-BnCCl-Hts, Figure 3) the phenyl substituent moves into conjugation with the forming double bond. The breaking C−H bond length is 1.291 Å, intermediate between that in *cis*-EtCCl-ts and $^{\mathrm{i}}$PrCCl-ts. The effect of phenyl substitution is to lower both the activation energy E_a and $\Delta G^‡$ by 6.0 kcal/mol, considerably more than either alkyl or halo groups. The 1,2-H shift transition state with the phenyl and chloro groups cis (*cis*-BnCCl-Hts), also shown in Figure 3, has the phenyl ring 27.2° out of the plane of the forming double bond due to a steric repulsion with the chlorine, and a higher activation energy of 8.5 kcal/mol, compared to 5.5 kcal/mol for the trans shift. Energies are given

TABLE 4: B3LYP/6-31G* Barriers to 1,2-H and 1,2-Ph Shifts in 1,2-Dichloroethylidene and 1-Chloro, 2-Fluoroethylidene in kcal/mol[a]

rearrangement	stationary points for E difference	E_a	E_a with ZPE	$\Delta G^\ddagger$	$\Delta S^\ddagger$ (e.u.)
cis-dichloroethylidne 1,2-H shift t.s.	*cis*-$ClCH_2CCl$-ts	11.6	9.9	10.2	−1.9
	syn-$ClCH_2CCl$-C_s	(10.3)	(8.5)	(8.8)	
trans-dichloroethylidene 1,2-H shift t.s.	*trans*-$ClCH_2CCl$-ts	14.5	12.6	13.4	−3.7
	anti-$ClCH_2CCl$-C_1	(12.8)	(10.9)	(11.7)	
cis-1-chloro, 2-fluoroethylidene 1,2-H shift t.s.	*cis*-FCH_2CCl-ts	9.9	8.2	8.4	−1.5
	syn-FCH_2CCl-C_s				
trans-1-chloro, 2-fluoroethylidene 1,2-H shift t.s.	*trans*-FCH_2CCl-ts	12.0	10.2	10.7	−2.4
	anti-FCH_2CCl-C_s	(10.7)	(9.0)	(9.4)	

[a] B3LYP/6-311G**//B3LYP/6-31G* energies in parentheses. $\Delta G^\ddagger$ and $\Delta S^\ddagger$ at 298 K.

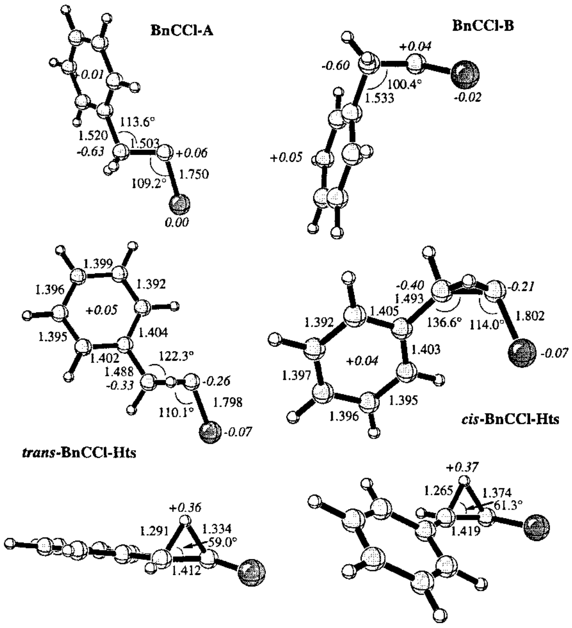


Figure 3. B3LYP/6-31G* geometries for lowest-energy carbene conformers and 1,2-H shift transition states for the rearrangement of benzylchlorocarbene.

in Table 5. The changes in charge at C_2 for the trans and cis 1,2-H shifts are +0.30 and +0.23.

We have also examined the singlet 1,2-Ph shift in benzylchlorocarbene for comparison with the 1,2-H shift. The geometry of the transition structure is shown in Figure 4, and energies are given in Table 5. Considerable aromaticity is retained in the phenyl ring in the transition state: the variation in C−C bond lengths is less than 0.042 Å, compared to 0.049 Å in a phenonium ion, computed at the same level. Less charge transfer from C_2 to C_1 occurs in the 1,2-Ph shift transition state compared to the 1,2-H shift; the NPA partial charge on C_2 increases +0.23 compared to +0.33 in the MeCCl 1,2-H shift. The activation energy for the 1,2-Ph shift is 9.5 kcal/mol, which is 4.0 kcal/mol greater than for the 1,2-H shift in benzylchlorocarbene but 2.0 kcal/mol less than the barrier to 1,2-H shift in methylchlorocarbene.

Methylbenzylchlorocarbene. To compare the influence of alkyl substitution on 1,2-H shifts and 1,2-Ph migrations, we located stationary points for the four possible 1,2-shift rearrangements of methylbenzylchlorocarbene (MeBnCCl). These are shown in Figures 4 and 5. The lowest energy conformer of the carbene (MeBnCCl-A) has the phenyl group face-on to the empty p-orbital, with an attractive interaction between the π-system and the empty orbital reducing the C_1−C_2−Ph bond angle to 98.7°. The chloro and methyl substituents are anti; the syn arrangement of these two groups (MeBnCCl-B) is 1.6 kcal/mol higher in energy (B3LYP/6-31G*). A third minimum was also located for this molecule that has the C_2−H bond aligned with the carbene p-orbital. This conformer (not shown) is 2.3 kcal/mol above MeBnCCl-A (B3LYP/6-31G*). Energies are reported in Table 6.

Both the trans and cis 1,2-H shifts in MeBnCCl have very early transition states (*trans*- and *cis*-MeBnCCl-Hts in Figure 5), with breaking C−H bond lengths of 1.266 and 1.274 Å, respectively. The forming double bonds are also quite long: 1.426 and 1.424 Å. In the trans transition state the phenyl ring approaches conjugation with the forming π-system, but steric interactions with the gem methyl substituent force it to lie 33.9° out of plane. The changes in charge at C_2 are +0.23 and +0.22 for the trans- and cis-1,2-H shifts, respectively. The activation energy for the trans-1,2-H shift is 5.1 kcal/mol, only 0.4 kcal/mol lower than that for benzylchlorocarbene and 1.7 kcal/mol lower than the 1,2-H shift in EtCCl. The cis 1,2-H shift transition state is higher in energy, with a barrier of 6.4 kcal/mol. The phenyl substituent in this transition structure is even further out of the plane of the forming alkene (56.8°).

The transition structures for the 1,2-Ph shifts in methylbenzylchlorocarbene are shown in Figure 4. The methyl-substituted transition state occurs earlier than that for the 1,2-Ph shift in BnCCl, as measured by a longer forming double bond (1.424 or 1.427 Å compared to 1.418 Å). The breaking and forming C−C bonds are both longer than in BnCCl, but the greater difference between their lengths also suggests an earlier transition state. There is less bond length alternation in the phenyl ring than in the unsubstituted reaction. In *cis*-MeBnCCl-Phts all the phenyl C−C bonds are within 0.017 of 1.4 Å. NPA charges at C_2 change from −0.40 (MeBnCCl-A) to −0.24 (cis-ts) or −0.20 (trans-ts), giving a change of only +0.16 to +0.20. A cis methyl substituent reduces the activation energy for the 1,2-Ph shift by 1.8 kcal/mol from that in benzylchlorocarbene, while a trans methyl group lowers the barrier by 1.3 kcal/mol, to 8.2 kcal/mol.

Triplet 1,2-Ph Shifts in Benzylcarbene. The 1,2-Ph shifts in triplet carbenes are more facile than 1,2-H shifts.[32b] To assess substituent effects, we have computed stationary points on the lowest triplet surface of benzylcarbene (BnCH), shown in Figure 6. The transition state for the triplet 1,2-Ph shift in BnCH is later than that for the singlet 1,2-Ph shift in BnCCl, with the breaking and forming C_1−Ph bonds 1.796 and 1.468 Å long, respectively (Figure 6). The final closed-shell alkene product is obtained after intersystem crossing at some point along the reaction path. On the triplet surface the reaction leads to a biradical, which is twisted 127.2° out of plane in the transition state. For the triplet reaction $E_a = 12.8$ kcal/mol while $\Delta G^\ddagger = 13.9$ kcal/mol. Spin density in the transition state, which was localized on C_1 in the carbene, is redistributed over the carbon skeleton with one electron on C_1 and one delocalized over C_2

TABLE 5: B3LYP/6-31G* Barriers to 1,2-H and 1,2-Ph Shifts in Benzylchlorocarbene in kcal/mol[a]

rearrangement	stationary points for E difference	E_a	E_a with ZPE	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$ (e.u.)
benzylchlorocarbene trans-1,2-H shift t.s.	*trans*-BnCCl−Hts	8.5	6.8	7.5	−3.3
	BnCCl-A	(7.3)	(5.5)	(6.2)	
benzylchlorocarbene cis-1,2-H shift t.s.	*cis*-BnCCl-Hts	11.0	9.5	9.8	−2.2
	BnCCl-A	(10.0)	(8.5)	(8.8)	
benzylchlorocarbene 1,2-Ph shift t.s.	BnCCl−Phts	9.5	9.2	10.5	−6.0
	BnCCl-A	(9.8)	(9.5)	(10.8)	

[a] B3LYP/6-311G**//B3LYP/6-31G* energies in parentheses. $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ at 298 K.

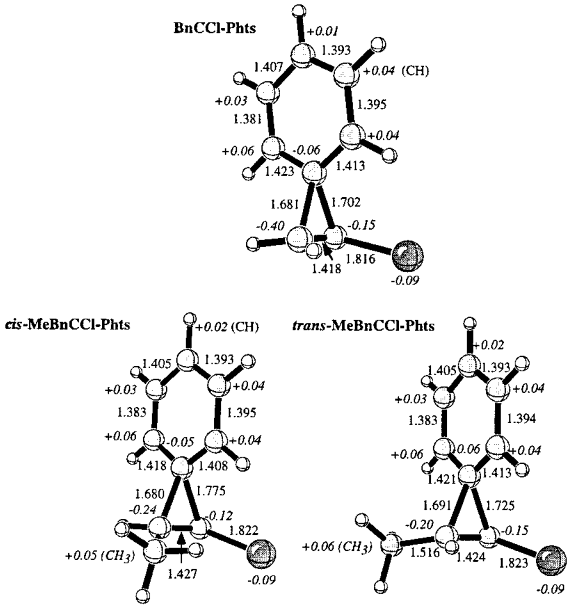


Figure 4. B3LYP/6-31G* 1,2-Ph shift transition structures for benzylchlorocarbene and α-methylbenzylchlorocarbene.

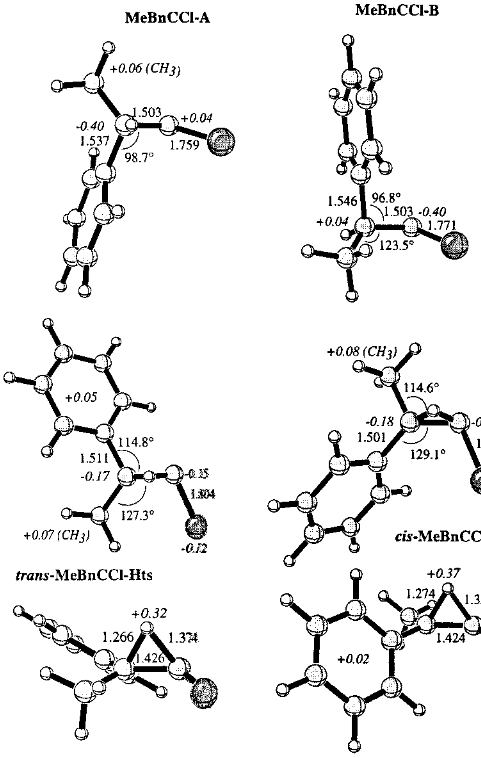


Figure 5. B3LYP/6-31G* geometries for lowest-energy carbene conformers and 1,2-H shift transition states for the rearrangements of α-methylbenzylchlorocarbene.

and the ortho and para positions of the migrating ring. The rearrangement occurs with a decrease of negative charge at C_2 and an increase at C_1, as for the singlet 1,2-shift reactions; charge at C_2 increases from −0.61 to −0.46.

A methyl substituent makes the triplet 1,2-Ph shift transition state earlier, as in the singlet rearrangement. Stationary point geometries for methylbenzylcarbene (MeBnCH) and its two 1,2-Ph shift transition states are shown in Figure 6 and energies are given in Table 7. The length of the breaking C_2−Ph bond decreases from 1.796 in ^{3}BnCH-Phts to 1.775 in *cis*-^{3}MeBnCH-Phts. The barrier is reduced from 12.8 to 10.7 kcal/mol. Once again, a cis substituent is better than a trans, leading to a very small preference (0.1 kcal/mol) for the cis-1,2-Ph shift.

1,2-Diphenylethylidene Rearrangements. Out of interest in calibrating how 1,2-Ph substituents might effect 1,2-H shifts in aryl carbenes studied in our laboratory, we have studied the rearrangement of 1-phenylethylidene (MeCPh) and of 1,2-diphenylethylidene (BnCPh) to *cis*- and *trans*-stilbene. Energies are given in Table 8. The barrier to 1,2-H shift in MeCPh is 8.2 kcal/mol, compared to approximately 1.2 kcal/mol for ethylidene.[4,38] E_a is reduced considerably by phenyl substitution at C_2, and the rearrangement of *trans*-BnCPh is predicted to have a barrier of only 3.3 kcal/mol.

Discussion

Alkyl and aryl substitution at C_2 is predicted to reduce the activation energy for 1,2-H shifts in carbenes. The hydride shift-like nature of the rearrangement, which leads to a decrease of electron density at the migration origin in the transition state, causes electron donors at C_2 to stabilize the transition state relative to the reactant. The discussion below will address whether substituent effects at the migration origin are additive for more than one substituent, how these effects depend on geometry, and how they depend on the type of carbene rearrangement. We evaluate Nickon's hypothesis about the inherent migratory preferences of H and Ph groups.

Alkyl Substitution. Alkyl substitution at C_2 lowers the barrier to 1,2-H shift and makes the transition state for the reaction earlier than in the unsubstituted system. This is consistent with expectations based on the Hammond postulate, since the exothermicities of the MeCCl, EtCCl, and ^{i}PrCCl rearrangements are 57.7, 61.4, and 64.1 kcal/mol, respectively, at the B3LYP/6-31G* level. The ability of the alkyl substituents to stabilize C_2 leads to less charge migration in the earlier transition states; the change in the NPA charge at C_2 is +0.33, +0.28 and +0.25 in the MeCCl, EtCCl, and ^{i}PrCCl rearrangements, respectively.

The effects of multiple methyl group substitution at C_2 are not strictly additive because substitution at the migration origin shows a syn/anti positional dependence. The preferred 1,2-H shift in EtCCl gives the *Z* alkene, and the syn methyl substituent at the migration origin reduces the activation energy by 4.7 kcal/mol from that in MeCCl. Addition of a second methyl group in the anti position, to give ^{i}PrCCl, further reduces E_a by 2.9

TABLE 6: B3LYP/6-31G* Barriers to 1,2-H and 1,2-Ph Shifts in Methylbenzylchlorocarbene in kcal/mol[a]

rearrangement	stationary points for E difference	E_a	E_a with ZPE	$\Delta G^\ddagger$	$\Delta S^\ddagger$ (e.u.)
methylbenzylchlorocarbene trans-1,2-H shift t.s.	*trans*-MeBnCCl−Hts	8.9	6.4	6.8	−1.7
	MeBnCCl-A	(7.6)	(5.1)	(5.5)	
methylbenzylchlorocarbene cis-1,2-H shift t.s.	*cis*-MeBnCCl−Hts	10.2	7.8	8.4	−2.7
	MeBnCCl-A	(8.7)	(6.4)	(7.0)	
methylbenzylchlorocarbene cis-1,2-Ph shift t.s.	*cis*-MeBnCCl−Phts	8.1	7.2	8.2	−4.3
	MeBnCCl-A	(8.5)	(7.7)	(8.7)	
methylbenzylchlorocarbene trans-1,2-Ph shift t.s.	*trans*-MeBnCCl−Phts	8.8	7.9	9.1	−5.1
	MeBnCCl-A	(9.1)	(8.2)	(9.4)	

[a] B3LYP/6-311G**//B3LYP/6-31G* Energies in Parentheses. $\Delta G^\ddagger$ and $\Delta S^\ddagger$ at 298 K.

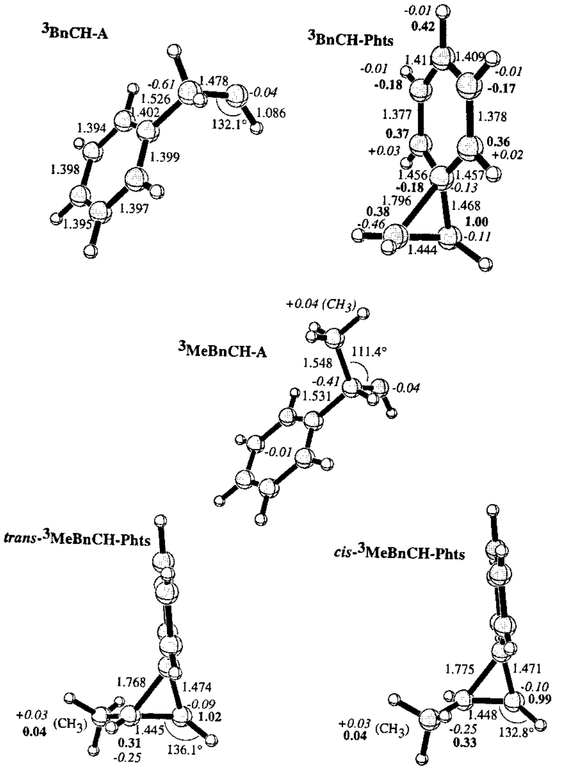


Figure 6. UB3LYP/6-31G* geometries for lowest-energy carbene conformers and 1,2-Ph shift transition states for the rearrangement of triplet benzylcarbene and triplet α-methylbenzylcarbene.

kcal/mol, a significantly smaller effect. If the initial methyl group is introduced trans to the chlorine it lowers E_a by 4.5 kcal/mol, with the subsequent addition of a cis substituent worth an additional 3.1 kcal/mol. Thus, the average effect of the first methyl group is to reduce the activation energy by 4.6 kcal/mol, and the average effect of the second is a further reduction of 3.0 kcal/mol. A "saturation" effect is evident, which makes addition of the first group more effective, in absolute terms, than the second.[39] In both cases, however, substitution in the cis position stabilizes the transition state by 0.2 kcal/mol more than at the trans.[40]

Shustov et al. have reported that the small preference for the cis 1,2-H shift in EtCCl (experimental product ratios Z:E = 81.7:18.3,[41] 78:22[42]) originates from an attractive interaction between the chlorine and methyl groups in the transition state and from C−H/C−Cl σ^* hyperconjugation.[33] We believe there are other contributing factors. First, structures computed at the B3LYP/6-31G* level, which reproduce the observed cis preference, give evidence for steric repulsion between the chlorine and methyl groups in the transition state. Second, the transition state for the 1,2-H shift in propylidene (EtCH) also shows a cis preference of 0.2 kcal/mol at the B3LYP/6-31G* level, in the absence of a chlorine substituent.

The cis selectivity may come from the better stereoelectronic interactions of a methyl substituent anti to the carbene lone pair. Because the cis preference is larger in the transition state than in the carbene or the product, we believe that it arises from the better electron-donating properties of a substituent in this position.

Halogen Substitution. An anti fluorine atom is a more effective bystander substituent than chlorine and reduces the 1,2-H shift activation energy by 2.5 kcal/mol from that in MeCCl; the barrier in $ClCH_2CCl$ is reduced by only 0.6 kcal/mol. The greater resonance electron-donating ability of fluorine, compared to chlorine, is reflected in the magnitude of its Hammett−Taft σ_R value (−0.31 for F vs −0.18 for Cl).[43] The Hammett−Taft σ_R value for a methyl group is only −0.13, however. Since neither halogen substituent, Cl or F (in the trans position), is as effective as a methyl group at stabilizing the transition state, σ_R is a poor overall indicator of the rate of rearrangement in C_2-substituted chlorocarbenes. This can be contrasted with C_1-substituted carbenes, where a good correlation of rearrangement rates with σ_R was found.[4] Inductive effects are probably also important in transition state stabilization at C_2.

Phenyl Substitution. Phenyl substituents at the migration origin are more effective than alkyl substituents at stabilizing 1,2-H shift transition states in those cases where steric factors do not prohibit conjugation of the aryl ring with the forming double bond. The trans-1,2-H shift in BnCCl has an activation energy of only 5.5 kcal/mol, which is 6.0 kcal/mol lower than in methylchlorocarbene. When steric factors prevent alignment of the phenyl group in the plane of the forming π-system, this substituent is less effective than a methyl group, however, reducing the activation energy for the cis-1,2-H shift in BnCCl by only 3.0 kcal/mol compared to MeCCl. The same effect is apparent in BnCPh: a trans phenyl group lowers the barrier by 6 kcal/mol, while a cis substituent only gives a 3 kcal/mol reduction.

The ideal alignment of a phenyl ring with the forming π system can also be disrupted by a second C_2 substituent. A geminal methyl substituent prevents the phenyl ring from achieving planarity, and the activation energy for the 1,2-H shift in MeBnCCl is consequently only 1.7 kcal/mol lower than in EtCCl. The preferred 1,2-H shift transition state, with the phenyl and chlorine groups trans, has the phenyl ring 34° out of plane; in the transition state with the phenyl and chlorine groups cis the ring is twisted 57° out of plane. The cis reaction has a barrier of 6.4 kcal/mol, only 0.4 kcal/mol lower than that in EtCCl. Steric effects clearly make substituent effects at C_2 nonadditive. A combination of nonoptimal alignment and saturation effects make the influence of a phenyl group on the barrier to rearrangement of EtCCl almost insignificant. Thus, despite the ability of an ideally positioned phenyl ring to accelerate 1,2-H shifts considerably more than a methyl sub-

TABLE 7: UB3LYP/6-31G* Barriers to Triplet 1,2-Ph Shifts in Benzylcarbene and Methylbenzylcarbene in kcal/mol[a]

rearrangement	stationary points for *E* difference	E_a	E_a with ZPE	$\Delta G^‡$	$\Delta S^‡$ (e.u.)
benzylcarbene 1,2-Ph shift t.s.	^{3}BnH−Phts	14.5	12.8	13.9	−4.8
	^{3}BnH-A	(14.5)	(12.8)	(13.9)	
methylbenzylcarbene cis-1,2-Ph shift t.s.	*cis*-^{3}BnH−Phts	12.1	10.5	11.0	−2.5
	^{3}BnH-A	(12.3)	(10.7)	(11.2)	
methylbenzylcarbene trans-1,2-Ph shift t.s.	*trans*-^{3}BnH−Phts	12.3	10.7	11.2	−2.5
	^{3}BnH-A	(12.5)	(10.8)	(11.4)	

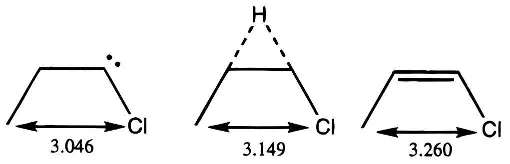
[a] UB3LYP/6-311G**//B3LYP/6-31G* Energies in Parentheses. $\Delta G^‡$ and $\Delta S^‡$ at 298 K.

TABLE 8: B3LYP/6-31G* Barriers to Singlet 1,2-H Shifts in Methylphenylcarbene and Benzylphenylcarbene in kcal/mol[a]

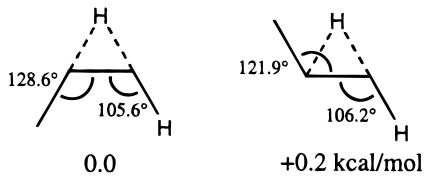
rearrangement	stationary points for *E* difference	E_a	E_a with ZPE	$\Delta G^‡$	$\Delta S^‡$ (e.u.)
1-phenylethylidene 1,2-H shift	PhCMe-ts	11.3	9.8	10.2	−2.5
	PhCMe	(9.8)	(8.2)	(8.6)	
benzylphenylcarbene cis-1,2-H shift t.s.	*cis*-BnCPh-ts	10.4	8.9	9.5	−2.6
	anti-BnCPh	(9.5)	(8.1)	(8/6)	
benzylphenylcarbene trans-1,2-H shift t.s.	*trans*-BnCPh-ts	6.1	4.4	5.0	−2.9
	anti-BnCPh	(5.0)	(3.3)	(4.0)	

[a] B3LYP/6-311G**//B3LYP/6-31G* Energies in Parentheses. $\Delta G^‡$ and $\Delta S^‡$ at 298 K.

SCHEME 2



C-Cl distances for EtCCl stationary points



B3LYP/6-31G* transition states for 1,2-H shifts in propylidene

stituent, two methyl groups are much more effective than one methyl and one phenyl group.

Singlet 1,2-Phenyl Shifts. Singlet 1,2-Ph shifts are also accelerated by alkyl substitution at C_2. While the origin of the effect appears to be the same as in the 1,2-H shift, the acceleration is smaller for the aryl shifts because the charge transfer from C_1 to C_2 is smaller. The change in charge at C_2 is +0.33 for the 1,2-H shift in MeCCl and +0.23 for the 1,2-Ph shift in BnCCl. Methyl substitution lowers the barrier for 1,2-Ph shift by about 1.5 kcal/mol, compared to 4.6 kcal/mol for the 1,2-H shift in MeCCl.

The structures of the two possible 1,2-phenyl shift transition states in MeBnCCl (Figure 4) are very similar to the one in BnCCl. Of the two rearrangements, the one to form the *Z* product, with the methyl and chlorine groups *cis*, is favored. The cis methyl substituent lowers the barrier to 1,2-Ph shift by 1.8 kcal/mol, while the trans effect is only 1.3 kcal/mol, using the 1,2-Ph shift in BnCCl as a reference. This is the same trend that is seen in the effects of alkyl substituents on the rates of 1,2-H shift rearrangements and probably shares the same origin.

Triplet 1,2-Ph Shifts. Triplet 1,2-Ph shifts are expected to show biradical character, and this is confirmed by examining the spin densities for the transition state in benzylcarbene. The spin density at C_2 increases from about zero in the carbene to 0.38 in the transition structure, where one spin unit is delocalized over this center and the phenyl ring. Similar charge redistribution between C_1 and C_2 occurs in the triplet 1,2-Ph shift, as in the singlet, but to a smaller extent. The change in the NPA charge at C_2 is +0.14 for the triplet BnCH rearrangement, compared to +0.23 for the singlet 1,2-Ph shift in BnCCl. The addition of a methyl substituent (to give ^{3}MeBnCH-Phts) reduces the spin at C_2 to 0.33 in the transition state, with 0.04 on the methyl group. The substitution does not reduce the change in charge at C_2, +0.16, which is actually slightly greater than in the unsubstituted case. The barrier is lower by 2.1 kcal/mol (16%) for the substituted rearrangement, and the transition state is earlier. The accelerating effect of a methyl group at C_2 seems to come primarily from stabilization of the unpaired electron on the forming diradical center, since the change in charge at C_2, which is reduced by substituents in singlet 1,2-H and 1,2-Ph shifts, does not occur here. Nevertheless, the relative acceleration that can be achieved upon methyl substitution is comparable in the singlet and triplet Ph shifts considered here.

Substituent Effects and Inherent Migratory Preferences. Abundant experimental evidence confirms that where 1,2-H and 1,2-Ph migration are both possible, singlet carbene rearrangements show a preference for hydrogen migration. For example, in the rearrangement of BnCCl, only *Z*- and *E*-chlorostyrene products are found.[44,45] It is clear from the data presented above, however, that bystander substituents have a large influence on rearrangement rates. Also, the barrier to phenyl migration is of the same order as the barrier to many 1,2-H shifts. It is interesting, therefore, to address the issues raised by Nickon:[19] to what extent do inherent migratory preferences dictate product formation, and to what extent are substituent effects responsible?

A comparison of the barriers to 1,2-H migration in MeCCl and 1,2-Ph migration in BnCCl, which gives the inherent migratory preferences without any influence from bystander substituents, shows a clear preference for migration of the phenyl group. The phenyl shift has a barrier of only 9.5 kcal/mol compared to 11.5 for the H migration. The free energy difference favors the phenyl migration by 1.4 kcal/mol. The smaller difference in free energy is due to the unfavorable entropic cost of aligning the 11 atoms of the large phenyl ring in the transition state, rather than just a single H. The entire rotational entropy of the phenyl ring is lost in the transition state in the highly organized spiro geometry.

Substituent effects may be responsible for the predominance of 1,2-H shift products seen in experimental results. In order

TABLE 9: Comparison of Calculated and Observed Activation Parameters (with ZPE Correction) in kcal/mol for 1,2-H Shifts in Alkylchlorocarbenes

carbene	exptl activation parameters	E_{act} B3LYP/6-31G*	E_{act} B3LYP/6-311G**//B3LYP/6-31G*
methylchlorocarbene	$E_a = 4.9$[a]	13.5	11.5
ethylchlorocarbene	$\Delta H = 4.89$[b]	8.2	6.8
propylchlorocarbene	$E_a = 3.64$[c]		
isopropylchlorocarbene	$E_a \approx 2$[c]	5.3	3.9
cis-1,2-dichloroethylidene	$\Delta G = 7.5$[d]	9.9	8.5
benzylchlorocarbene	$E_a = 4.5$[e]	6.8	5.5
	$E_a = 5.78$[f]		
2-phenylethylchlorocarbene	$E_a = 2.85-3.0$[c]	6.4	5.1

[a] LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877−6878. [b] Dix, E. J. Ph.D. Thesis, University of Rochester, New York, 1994. [c] Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1996**, *118*, 8098−8101. [d] Bonneau, R.; Liu, M. T. H.; Kim, K. C.; Goodman, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 3829−3837. [e] Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1996**, *118*, S **1990**, *112*, 3915−3919. [f] Liu, M. T. H.; Bonneau, R.; Wierlacher, S.; Sander, W. *J. Photochem. Photobiol.* **1994**, *84*, 133−137.

for the activation energy for the 1,2-H shift in benzylchlorocarbene to be lower than that for the 1,2-Ph shift, the phenyl substituent must accelerate the H shift by at least 2.0 kcal/mol. Evidence presented above indicates that a single phenyl substituent can be worth between 3.0 and 6.0 kcal/mol. Thus, in benzylchlorocarbene, where ideal alignment of the phenyl ring is possible, the 1,2-H shift is preferred over the 1,2-Ph shift by 4.0 kcal/mol (equal to the ideal accelerating power of the phenyl ring of 6.0 kcal/mol minus the preferential inherent migratory preference of Ph of 2.0 kcal/mol). The free energy preference is larger, 4.6 kcal/mol, as expected in view of the lower entropy of activation for the phenyl shift. Another factor that could contribute to the more favorable 1,2-H than 1,2-Ph shifts observed experimentally is quantum mechanical tunneling. This has been computed to accelerate the 1,2-H shift in MeCCl by about 11 times at 298 K and is not expected to contribute to the rate of 1,2-Ph shift.[31,46]

Notably, in situations where the phenyl ring is not as effective as a substituent, as in MeBnCCl, the preference for 1,2-H over 1,2-Ph migration is smaller. In MeBnCCl the 1,2-H shift is favored by about 2.6 kcal/mol, while the free energy preference is 3.2 kcal/mol. The preference for H is greater than would be expected based purely on the accelerating power of the nonplanar phenyl ring (only 1.7 kcal/mol) since the bystanding effect of the methyl group is more effective at lowering the 1,2-H shift barrier than the 1,2-Ph shift barrier.

On the basis of these results, it is possible that the rearrangement of 2,2-diphenylmethylchlorocarbene might give significant amounts of 1,2-Ph shift. In that case, steric interactions between geminal C_2 phenyl groups would prevent effective stabilization of a 1,2-H shift transition state, while good alignment of a single phenyl bystander substituent with the forming π-system could accelerate the phenyl rearrangement significantly.

Comparison of Alkylchlorocarbene Results to Experimental Data. There are difficulties in comparing the results reported above to experiment. First, accurate experimental measurements of carbene reactivity are very challenging. (1) As repeatedly demonstrated by Platz, any detection of carbene reactivity is complicated by the chemistry of excited-state precursors that can give the same rearrangement products.[12,47] Experiments involving the trapping of carbenes with pyridine[48] or the use of photoacoustic calorimetry to resolve individual reaction steps[3] are required to separate the contributions of carbenes and precursors in any measurement of absolute rate constants. (2) It has been demonstrated that azine formation, which results from the addition of a carbene to a diazo or diazirine precursor, may compete with intramolecular carbene rearrangement.[49] Calculations by Shustov and Liu indicate that the addition of methylene or methylchlorocarbene to diazirine is effectively barrierless at the B3LYP/6-31+G* and MP2/6-311+G** levels.[50] Platz et al. have also pointed out the significance of reaction with solvent.[51] In cases where these intermolecular processes contribute to the depletion of carbene, even direct spectroscopic observation of carbenes may not give accurate rate constants. (3) As evident from the low barriers computed for many of the rearrangements discussed here, 1,2-H and 1,2-Ph shifts may be very fast. In particular, the fast rearrangements of ^{i}PrCCl and MeBnCCl are too rapid at room temperature for the time resolution available in conventional laser flash photolysis experiments.[6] The characterization of rearrangements at low temperature and extrapolation of rates for comparison to other reactions depends on knowledge of the enthalpy and entropy of reaction, which are difficult to determine accurately.

Table 9 compares our results at the B3LYP/6-31G* and B3LYP/6-311G**//B3LYP/6-31G* levels to experiment. As has previously been noted and discussed,[46,52] large discrepancies are apparent between the low activation energy of 4.9 kcal/mol measured for methylchlorocarbene and our computed values of 11.5 kcal/mol. This has been attributed to the role of quantum mechanical tunneling, but corrections for this process are not large enough to bring theory and experiment into quantitative agreement.[31,46] Bimolecular reactivity, inadvertently attributed to carbene rearrangement, may contribute to the difference; investigations into this are ongoing in our laboratory and in others. The computed activation energies for other carbene rearrangements are also systematically higher than the measured values. This could be the result of inaccuracies in the calculations; the larger basis set 6-311G** is seen to correct the barriers in the right direction.

Table 9 shows that the DFT calculations capture the experimental trends, although not the quantitative differences, between the activation energies for different rearrangements. A notable difference between experiment and theory comes from Liu and Bonneau's report that the addition of a methyl group to BnCCl lowers E_a by about 2.9 kcal/mol.[33] In contrast, we find a value of only 0.4 kcal/mol for the difference in activation energy between BnCCl and MeBnCCl. Computed structures indicate that the addition of a methyl group to benzylchlorocarbene disrupts the ideal planar transition state. The experimental result implies that addition of a methyl group to BnCCl is as favorable as the addition of a methyl group to EtCCl.

A common conclusion of the experimental and theoretical substituent effect studies, however, is that the difference in rates results primarily from changes in the enthalpy, not the entropy, of activation. While calculations do suggest that more substi-

TABLE 10: Summary of Substituent Effects[a]

substituent	carbene	reaction	Δ charge at C_2 in parent	position	ΔE_a	$\Delta\Delta G^{\ddagger}$
methyl	XC:Cl	H shift	+0.33	syn	4.7	5.2
			+0.33	anti	4.5	4.6
		singlet Ph shift	+0.23	syn	1.8	2.1
			+0.23	anti	1.3	1.4
	XC:H	singlet Ph shift	+0.09	syn	no barrier	
			+0.09	anti	0.0	−0.1
		triplet Ph shift	+0.14	syn	2.1	2.7
			+0.14	anti	2.0	2.5
Cl	XC:Cl	cis-H shift	+0.33	syn	3.0	3.4
		trans-H shift	+0.33	anti	0.6	0.5
F	XC:Cl	cis-H shift	+0.33	syn	5.3	5.8
		trans-H shift	+0.33	anti	2.5	2.8
phenyl	XC:Cl	H shift	+0.33	syn	3.0	3.4
			+0.33	anti	6.0	6.0
	XC:Ph	H shift	+0.28	syn		
			+0.28	anti		

[a] The reduction of the activation energy or free energy of activation by a substituent at C_2 is given in kcal/mol. Energies were computed at the B3LYP/6-311G**//B3LYP/6-31G* level and include ZPE correction.

tuted reactions with earlier transition states have smaller $\Delta S^{\ddagger}$'s, the computed $\Delta\Delta G^{\ddagger}$'s correlate well with $\Delta\Delta H^{\ddagger}$'s. This is in agreement with the conclusions of Liu et al. based on low-temperature laser flash photolysis results.[6]

Conclusions

Table 10 summarizes the computed substituent effects on the barriers to 1,2-H and 1,2-Ph shifts in all carbenes studied. The acceleration of 1,2-H shift reactions by C_2 substituents follows the order Ph > Me > F > Cl > H. With the exception of phenyl groups, where steric effects dominate, syn substituents are more effective than anti at stabilizing the transition state. For Cl and F, this is because of hyperconjugative interactions. For alkyl groups this has been explained in terms of the bond hybridization and polarization that best allows electron donation to C_2.

The magnitudes of substituent effects also depend on the type of carbene rearrangement. Singlet 1,2-H shifts are accelerated the most by a methyl group, followed by singlet and triplet Ph shifts, in that order. Singlet 1,2-H shifts show a greater change in the C_2 NPA charge (+0.33 for MeCCl) than singlet 1,2-Ph shifts (+0.23 for BnCCl), while triplet Ph shifts appear to benefit from stabilization of developing spin at C_2 by an alkyl group.

As proposed by Nickon, we find that the identity of the bystanding substituent can be more significant for determining the products of competitive carbene rearrangements than are intrinsic migratory aptitudes. According to results presented here, the exclusive 1,2-H shift observed in BnCCl comes not from a migratory preference for H over Ph, but from the greater ability of a phenyl substituent to accelerate 1,2-H shift than of an H to accelerate 1,2-Ph shift. Tunneling in the 1,2-H shifts may also play some small role in determining the extent of the preference. It is clear that bystander substituents can have an important influence on rearrangement rates and should be carefully considered when making kinetic analogies between carbenes.

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Supporting Information Available: Listings of energies for all compounds (in hartrees) (8 pages). See any current masthead page for ordering and Internet access instructions.

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