Perfluorocarbenes Produced by Thermal Cracking. Barriers to Generation and Rearrangement

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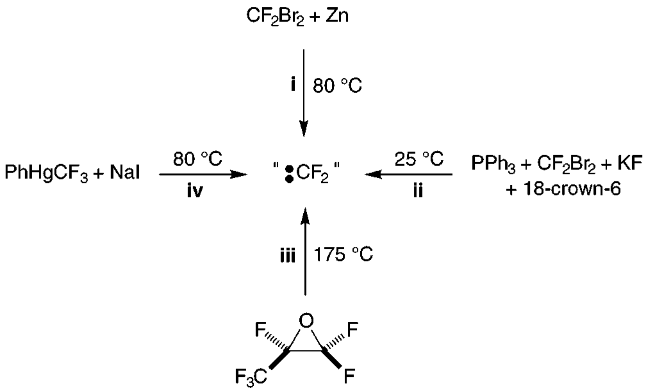
Thermal crackings of substituted oxiranes to generate various perfluoroalkylcarbenes are examined using ab initio density functional theory. Such reactions are generalizations of a current technology for the preparation of difluorocarbene. Barriers for the generation of fluoro(perfluoroalkyl)carbenes by this approach are computed to be higher than those for generation of difluorocarbene; the difference is attributed primarily to the lower stability of the respective singlet carbenes. Once generated, however, the carbenes are reasonably stable with respect to unimolecular rearrangement, so that high selectivity for reaction with olefins, such as might be present in an unsaturated polymer, may be expected under typical experimental conditions. With respect to rearrangements of perfluorocarbenes, 1,2-alkyl shifts are lowest in energy, 1,2-fluorine atom shifts are higher, and 1,3-fluorine atoms shifts are highest of all; this ordering reflects the relative orbital energies of the σ bonds broken in the respective migrations. In instances where thermal conditions required for oxirane cracking may be incompatible with other functionalities in the reaction medium, theory predicts that extrusion of SiF_4 from perfluorosilylalkanes may be an attractive alternative for perfluorocarbene generation.

Introduction

The incorporation of fluorine into macromolecules can have profound effects on the resultant material properties. The enhanced chemical resistance, reduced surface energy, and high temperature performance of fluoropolymers is remarkable when compared to their hydrocarbon analogues,[1] and this has led to intense research efforts geared toward the incorporation of fluorine into synthetic and biological macromolecules.[2] Although, most fluorinated polymers are generated from corresponding fluorinated monomers, postpolymerization fluorination methods are available.[3−5] The fluorination of polymers offers unique opportunities for the design of polymers with specific properties, particularly with respect to phase separation in heterogeneous systems such as block copolymers.[6]

A relatively new and convenient technique for introducing fluorocarbon functionality into macromolecules is the perfluorocyclopropanation of double bonds in polydienes by difluorocarbene generated in situ.[7,8] Difluorocarbene can be conveniently generated via a number of techniques,[9] and Scheme 1 shows four routes to difluorocarbene (or some difluorocarbenoid species): (i) a Simmons−Smith-like procedure,[10] (ii) a modified Burton procedure,[11] (iii) thermolysis of hexafluoropropylene oxide (HFPO),[12] and (iv) the Seyferth method.[13] The use of route iii for the fluorination of macromolecules has recently been demonstrated by one of us to be particularly useful for the preparation of model fluorinated homopolymers and block copolymers.[8]

Scheme 1



A valuable extension of the current technology would allow for the preparation of model fluorinated polymers that contain *more* than two fluorine atoms per repeat unit. Ideally, the systematic and controlled incorporation of fluorine could be accomplished using higher homologues of HFPO. Two issues arise in this context, however. First, the energy required to crack out the intermediate carbene must not be so high that the conditions would also be expected to lead to its rapid

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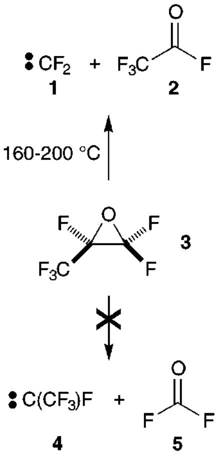
(unimolecular) destruction by, say, rearrangement. Second, for the carbene to selectively modify the polymer, it is critical that it react out of its singlet state. While fluoro(perfluoroalkyl)carbenes would be expected to be ground-state singlets lying well below their corresponding triplet states,[14] that is unlikely to be the case for bis(perfluoroalkyl)carbenes.[15,16]

In this paper we use density functional theory (DFT) to computationally predict the likely utility of two different cracking reactions for the generation of fluoro(perfluoroalkyl)carbenes. In particular, we consider the epoxide cracking mentioned above and a tetrafluorosilane extrusion method.[17] Particular attention is paid to the relative energetics of carbene formation, addition, and unproductive rearrangement reactions.

Theoretical Methods. Most geometries were optimized using the gradient-corrected functionals of Becke[18] for exchange and of Perdew and Wang[19] for correlation (BPW91) with the correlation-consistent polarized valence double-ζ[20] (cc-pVDZ) basis set. At this level, analytic frequency calculations were performed to verify the nature of all stationary points (minima and transition state structures), and these frequencies were used to compute zero-point vibrational energies (ZPVE) and 298 K thermal contributions to the enthalpies and standard-state (1 atm) gas-phase free energies of all species using standard statistical mechanical approximations.[21] In cases where multiple rotameric minima exist, the lowest energy rotamer was employed in all calculations; however, rotamer energy differences were always quite small. A few geometries were optimized at the restricted Hartree–Fock (RHF) level using the 3-21G basis set,[22] as further explained in the next section. Other levels of gas-phase theory were also employed for select calculations as described in the Appendix.

Standard-state (1 M solute in gas phase and solution) solvation free energies ΔG°_S in diethyl ether (dielectric constant $\epsilon = 4.24$)[23] were computed for selected structures using the SM5.42R/BPW91/6-31G* solvation model[24,25] based on Class IV charges[26] obtained with the 6-31G* basis set.[27,28] These calculations employed gas-phase BPW91/cc-pVDZ geometries (the “R” in SM5.42R implies that the model was designed to use gas-phase geometries kept *R*igid in the liquid solution phase). All calculations were carried out with a locally modified version of the Gaussian 94 electronic structure program suite.[29,30]

Scheme 2



Results and Discussion

Difluorocarbene (**1**) and trifluoroacetyl fluoride (**2**) are generated from the thermal cracking of HFPO (**3**) as depicted in Scheme 2. The reactivity of **1** is relatively uncomplicated as it is an extremely stable singlet that is not prone to unimolecular decomposition.[31−41] Interestingly, the alternative cracking pathway, which would generate fluoro(trifluoromethyl)carbene (**4**) and carbonyl difluoride (**5**), is not accessed, as judged by the absence of products derived from reactions with **4**. The design of alternative systems to permit the generation of fluoro(perfluoroalkyl)carbenes via epoxide cracking would be a useful extension of this technology for incorporation of more diverse fluorinated functionality into unsaturated polymers.[42]

In this section, we first characterize the thermal cracking reactions of **3**. We then characterize *trans*-2,3-difluoro-2,3-bis(trifluoromethyl)oxirane (**6**) cracking, where symmetry requires that **4** be the only carbene generated. Next, we examine the relative facility of the 1,2-fluorine shift in **4**, both in the gas phase and in ethereal solution. We then briefly consider the thermal cracking of oxiranes

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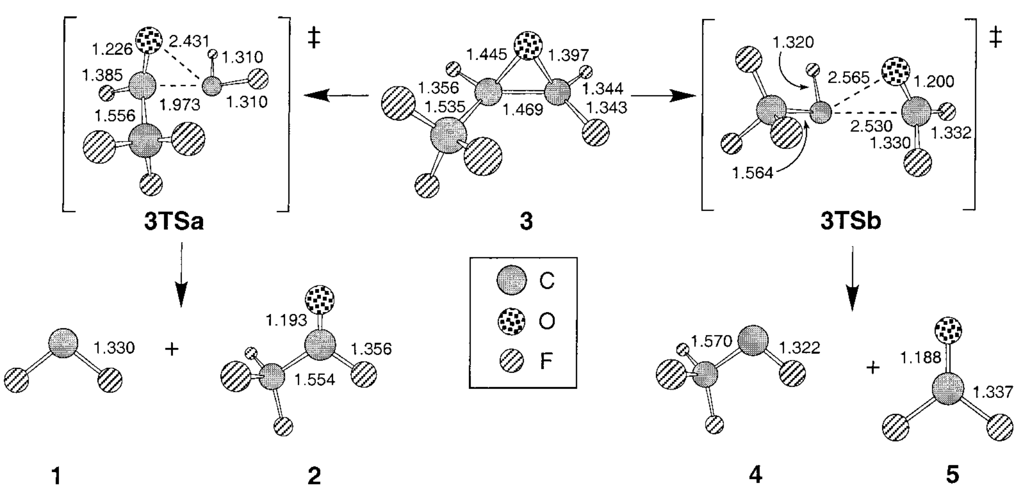
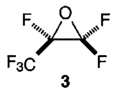
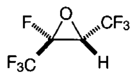
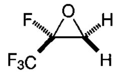
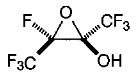
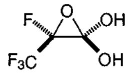


Figure 1. Optimized structures for stationary points **1**–**5** at the BPW91/cc-pVDZ level. Selected heavy-atom bond lengths (Å) are provided.

Table 1. Cracking Barriers and Exoergicities (kcal/mol) for Fluorinated Epoxides

			Relative energies			
			2 + carbene		**4** + carbonyl	
	Theoretical Level[a]		Barrier	Products	Barrier	Products
 **3**	BPW91/cc-pVDZ//HF/3-21G	ΔE			44.9	
	BPW91/cc-pVDZ	ΔE	35.3	30.9	51.4	53.1
		ΔG°_{298}	32.0	14.6	46.7	36.9
 **6**	BPW91/cc-pVDZ//HF/3-21G	ΔE			50.4	
	BPW91/cc-pVDZ	ΔE			57.4	58.9
		ΔG°_{298}			52.1	41.0
 **8**	BPW91/cc-pVDZ//HF/3-21G	ΔE			69.5	
 **9**	BPW91/cc-pVDZ//HF/3-21G	ΔE			47.5	
 **10**	BPW91/cc-pVDZ//HF/3-21G	ΔE	9.5		32.9	

[a] Epoxide absolute energies (h) for this column are: –788.522 96, –788.527 15, –788.524 75, –1026,304 79, –1026.311 57, –1026.301 43, –590.046 12, –1002.295 22, –740.501 11. These energies define the relative zero for each reaction coordinate.

bearing alternative functional groups designed to lower the cracking barrier and also the alternative process of silane extrusion from a perfluorosilylalkane. Finally, we consider various carbene rearrangements available to larger perfluorocarbenes.

In the interests of conciseness, most of the following discussion refers only to the BPW91/cc-pVDZ level. The choice of this level was motivated by its quantitative accuracy in comparison with various other high levels of theory for benchmark systems as further described in the Appendix to this article.

Thermolysis of HFPO (3). The asymmetric substitution in **3** allows thermal cracking to follow either of two pathways. The products can be either **1** and **2** or **4** and **5**. Figure 1 presents computed structures for **3**, products **1** and **2**, products **4** and **5**, and the alternative transition state (TS) structures leading to these products (**3TSa** and **3TSb**, respectively). Table 1 compares the relative energies associated with these two competing pathways. The BPW91/cc-pVDZ results indicate that the potential barrier for cracking to give products **1** and **2** is 16.1 kcal/mol lower than the barrier for cracking out the larger carbene **4** together with **5**. This difference in barrier heights reflects a significant portion of the difference in reaction endoergicities; the reaction yielding **1** and **2** is endoergic by 14.6 kcal/mol, which is 22.2 kcal/mol less

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(42) A simple and general preparative route for the formation of perfluorinated epoxides has been reported; see (a) Kolenko, I. P.; Filyakova, T. I.; Zapevalov, A. Ya.; Lure, É.P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, *11*, 2509. In addition, work has been reported on the thermolysis of higher perfluorinated epoxides, and although in general these compounds are more thermally stable than **3**, the intermediacy of fluoro(perfluoroalkyl)carbenes and bis-perfluoroalkyl carbenes was inferred from structural analysis of the thermolysis products. For example, see (b) Kagramanov, N. D.; Kutin, A. A.; Peschanskii, N. V.; Zapevalov, A. Y.; German, L. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1991**, *7*, 1497, and (c) Coe, P. L.; Sellars, A.; Tatlow, J. C. *J. Fluorine Chem.* **1985**, *27*, 71.

endoergic than the analogous reaction yielding **4** and **5.** In keeping with the Hammond postulate,[43] Figure 1 indicates transition state structure **3TSb** for the latter (more endoergic) reaction to be significantly more product-like than is the case for **3TSa**: the breaking C−C and C−O bond lengths in **3TSb** are 0.557 and 0.134 Å longer, respectively, than those in **3TSa**.[44]

The calculated barrier height for the thermolysis of **3** (35.3 kcal/mol) is in excellent agreement with an experimentally measured Arrhenius activation energy of 36.3 kcal/mol.[45] Accounting for thermal contributions to the standard-state free energy, the cracking reactions both become about 16 kcal/mol less endoergic at 298 K (as a result of dissociation producing two molecules from one, which is favorable entropically), and the activation free energies are reduced by 3−5 kcal/mol compared to the barrier heights. The *difference* in activation free energies for the production of **1** and **2** relative to **4** and **5** remains a substantial 14.7 kcal/mol, rationalizing why **3** is not a useful precursor for the preparation of **4**. Carbene stability is the primary contribution to the difference in endoergicities, and hence barrier heights, for these two reactions. A variety of effects contribute to **1** being a very stable singlet, in particular π conjugation.[32,33,38,41] Replacement of one fluorine by a trifluoromethyl group essentially annihilates about half of that stabilization.[46] An obvious approach to overcome this intrinsic difference in stabilities is to employ the epoxide of perfluoro-2-butene, where symmetry requires that cracking produce the desired carbene (**4**).

Thermolysis of 2,3-Difluoro-2,3-bis(trifluoromethyl)oxirane (6). For simplicity, we consider here only the trans isomer of **6**. This stereoisomer would derive from the epoxidation of the more thermodynamically stable *E* isomer of perfluoro-2-butene. Figure 2 presents computed structures for **6** and the transition state **6TS** leading to products **2** and **4** (structures for **2** and **4** are found in Figure 1). Table 1 details the relative energies associated with this thermal cracking. The BPW91/cc-pVDZ results indicate that the potential barrier for the cracking of **6** is 6 kcal/mol higher than the analogous pathway producing **4** from **3** via **3TSb**. As expected[43] given its higher energy relative to reactants, **6TS** is more product-like than **3TSb**—the breaking C−C and C−O bonds are 0.013 and 0.172 Å longer, respectively, in the former TS.

The predicted difference in barrier heights between **3TSb** and **6TS** is almost exactly the same as the difference in reaction endoergicities, reflecting the somewhat greater stability of **5** relative to its antecedent epoxide compared to **2** relative to its antecedent epoxide. Accounting for thermal contributions, the standard-state free energy of activation for cracking of **6** is predicted to be 52.1 kcal/mol. One would expect rather high reaction temperatures to be required for this cracking to proceed at a useful rate. In the absence of alternative decomposition pathways, however, nothing prevents this process.

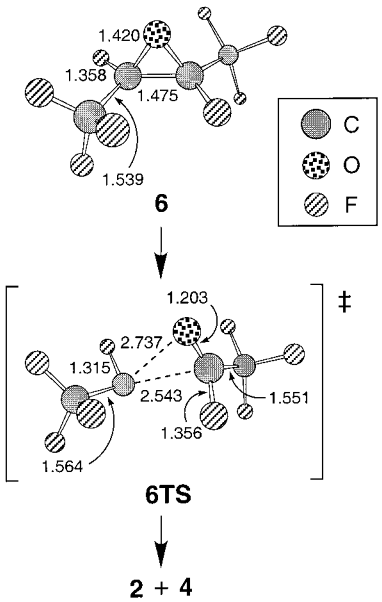

Figure 2. Optimized structures for stationary points **6** (C_2) and **6TS** at the BPW91/cc-pVDZ level. Selected heavy-atom bond lengths (Å) are provided.

1,2-Fluorine Shifts. A separate issue with respect to the potential utility of carbene **4** does arise. Unlike **1**, carbene **4** can undergo thermal rearrangement, and this unimolecular process might compete effectively with bimolecular addition reactions. The transition state structure **4TS** for 1,2-fluorine migration in **4** has been located at the BPW91/cc-pVDZ level. Selected geometric information is presented in Figure 3 and energetic details are presented in Table 2. Product tetrafluoroethylene is predicted at this level of theory to be lower in potential energy and standard-state free energy by 44.0 and 41.1 kcal/mol, respectively. Despite this large exoergicity, the migration still has a significant barrier of about 25 kcal/mol. This is quite similar to the situation predicted for the analogous 1,2-fluorine shifts in 2,2,2-trifluoroethylidene to give trifluoroethylene[16] and in difluorovinylidene to give difluoroacetylene.[47] The 1,2-fluorine shift in 2,2,2-trifluoroethylidene, which is most closely related to that examined here, is predicted to have a rearrangement barrier height (including zero-point energy) of 21.5 kcal/mol at the QCISD(T)/6-311G(2d,2p)//MP2/6-31G** level[16] (note that this calculation corrected a prior prediction[48] based on incorrect transition-state structures and is also probably more accurate than a prior estimate[49] of 29 ± 4 kcal/mol derived from a rather complex interpretation of various experimental results). Thus, fluorine substitution for hydrogen at the carbene carbon is predicted to raise the rearrangement barrier by roughly 4 kcal/mol.

Note that although the barrier for rearrangement of **4** is nearly 30 kcal/mol lower in energy than the cracking

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[43] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

[44] In the reaction producing **4** and **5** the potential energy of **3TSb** is *lower* than the sum of the product potential energies. While this may appear paradoxical, it reflects the presence of a weakly stable dipole−dipole complex between the two fragments just past the cracking transition state—a situation quite common in gas-phase reactions. The energy required for dissociation of this complex is slightly higher than the activation energy required for addition of the carbene across the C═O double bond (i.e., the reverse of cracking) to give **3**.

[45] Kennedy, R. C.; Levy, J. B. *J. Fluorine Chem.* **1976**, *7*, 101.

[46] Computations predict, and experimental studies infer, that a hydrogen atom and a trifluoromethyl group have roughly the same stabilizing effect (which is to say, none at all) on a carbene; see (a) Dixon, D. A. *J. Phys. Chem.* **1986**, *90*, 54. (b) O'Gara, J. E.; Dailey, W. P. *J. Am. Chem. Soc.* **1992**, *114*, 3581. (c) Seburg, R. A.; McMahon, R. J. *J. Org. Chem.* **1993**, *58*, 979. A phenyl substituent, on the other hand, is weakly stabilizing; see (d) Cramer, C. J.; Dulles, F. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1994**, *116*, 9787 and references therein.

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[48] So, S. P. *J. Phys. Chem.* **1993**, *97*, 11908.

[49] Holmes, B. E.; Rakestra, D. J. *J. Phys. Chem.* **1992**, *96*, 2210.

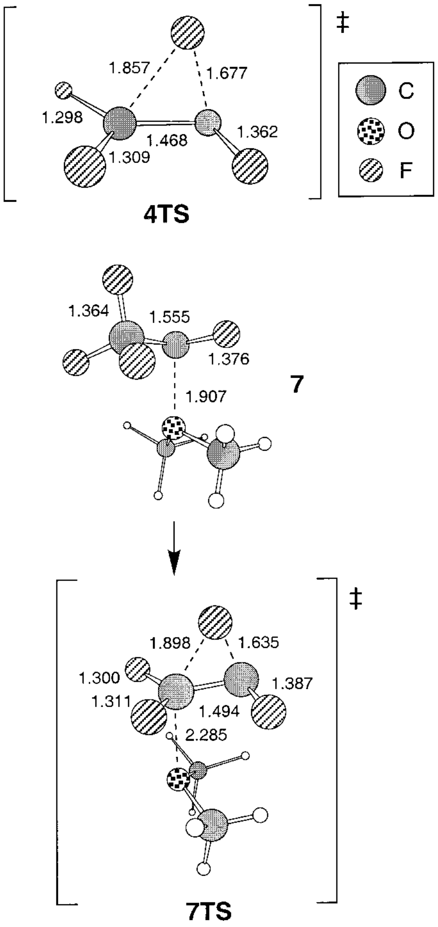

Figure 3. Optimized structures for stationary points **4TS**, **7**, and **7TS** at the BPW91/cc-pVDZ level. Selected heavy-atom bond lengths (Å) are provided.

barrier to produce **4** from **6**, this does not in any way mitigate against the utility of **6** as a possible source for generating **4**. Classical transition state theory[50] indicates that a gas-phase unimolecular rearrangement should proceed with a first-order rate constant of roughly $10^{14}\exp(-\Delta G^{\ddagger}/RT)$ s^{-1}; at 500 K a barrier of 25 kcal/mol corresponds to a rate constant of about 10^{3} s^{-1}. Carbene insertion reactions into alkenes, on the other hand, proceed with very low barriers.[51−53] Absolute barrier heights for low-barrier reactions are difficult to determine experimentally—for the highly stabilized carbene **1**, the barrier height for addition to tetrafluoroethylene has been measured in the gas phase to be about 6 kcal/mol.[54] Less-stabilized carbenes have still lower barriers. For instance, Arrhenius plots of the reaction of chloro(phenyl)carbene with various olefins give activation energies on the order of −1 to 1 kcal/mol.[55] In the case of fluoro(phenyl)carbene, which should probably be slightly *less* reactive than **4**,[46] typical bimolecular rate constants measured at 300 K are on the order of 10^{6} to 10^{8} M^{-1} s^{-1}.[56] This implies, conservatively, that if olefin concentration is kept above about 0.1 M, 99+% of **4** would be expected to react in a productive fashion. Viscosity of the reaction medium must also be considered, of course, since that affects the diffusion rate for the bimolecular reaction. In previous work one of us showed that concentrations of polydiene double bonds as high as 1.26 M in cyclohexane could be difluorocyclopropanated without any decrease in reaction efficiency.[8]

Besides viscosity, other effects associated with the solvent used as a reaction medium may affect the relative reaction rates. In analyzing solvation effects, one should consider first the possibility of specific carbene−solvent interactions. In particular, ethereal solvents can interact in a donor−acceptor fashion to generate ylide-like carbene-ether complexes.[53] Figure 3 provides the structure of the complex (**7**) formed between **4** and dimethyl ether. The complexation energy is predicted to be −13.1 kcal/mol at the BPW91/cc-pVDZ level; this large interaction energy is consistent with the short distance between the carbene carbon and the ether oxygen (1.907 Å). Moreover, the ylide-like character of the complex is manifest in the significant decrease in π interaction between the carbene carbon and the attached fluorine atom as judged by the 0.054 Å increase in that bond length.

Entropic effects almost exactly counterbalance the interaction energy, so that the standard-state (1 atm) free energy of complexation is +0.1 kcal/mol in the gas phase. Bulk solvation effects might be expected to play a significant role on this equilibrium as well, since **7** is substantially more polar than its uncomplexed fragments. Self-consistent reaction field calculations using the SM5.42R/BPW91/6-31G* solvation model[24,25] for diethyl ether (as a generic ethereal solvent) give absolute standard-state solvation free energies of −1.9, +1.4, and −3.2 kcal/mol for dimethyl ether, **4**, and **7**, respectively, so the net complexation standard-state (1 M) free energy in solution is predicted to be −4.5 kcal/mol (this includes −1.9 kcal/mol for the change in standard state from 1 atm to 1 M).

For a typical ethereal solvent, the concentration of ethereal oxygen atoms is on the order of 20 M (i.e., considerably higher than the 1 M standard state used for the free energy calculations above), which, in combination with the standard-state complexation free energy in solution, would render the uncomplexed carbene roughly 6.3 kcal/mol higher than the ylide in chemical potential. Thus, the 1,2-fluorine shift in an ethereal solvent, if it proceeds from the uncomplexed carbene, will proceed with an effective barrier 6.3 kcal/mol higher than that predicted for the gas phase. Of course, the ylide itself might have a lower barrier for the 1,2-fluorine shift. We have located the TS structure for this process (**7TS**, Figure 3) and compute the barrier to be about 4 kcal/mol higher than the same rearrangement for the free carbene—bulk solvation does not significantly affect this difference at the SM5.42R level (Table 2).

These data imply that if *addition* of the carbene fragment of the ylide across a double bond proceeds with a *smaller* increase in barrier height than is predicted for ylide rearrangement, ethereal solvents will further increase the likelihood of productive reaction of **4**. If, on the other hand, the increase in barrier height for addition of the ylide is more than 2 kcal/mol *larger* than for rearrangement, the reaction will simply proceed via prior

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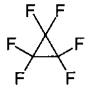
Table 2. Rearrangement Barriers and Associated Exoergicities (kcal/mol) for Fluorinated Carbenes at the BPW91/cc-pVDZ Level

Carbene[a]	Rearrangement		Barrier	Product	Exoergicity
4	1,2-F shift	ΔE	24.8	$F_2C{=}CF_2$	−44.0
		ΔG°_{298}	24.9		−41.1
7	1,2-F shift	ΔE	30.5	$F_2C{=}CF_2$	[b]
		ΔG°_{298}	29.0	• Me_2O	
		ΔG°_{298}(sol)[c]	29.3		
11	1,2-F shift	ΔE	25.8	$CF_3CF{=}CF_2$	−58.5
		ΔG°_{298}	25.9		−56.5
11	1,2-CF_3 shift	ΔE	18.2	$CF_3CF{=}CF_2$	−58.5
		ΔG°_{298}	18.5		−56.5
11	1,3-F shift	ΔE	36.3		−30.3
		ΔG°_{298}	36.4		

[a] Absolute energies [free energies] (h) for **4**, **7**, and **11**, respectively, which define their reaction coordinate zeros of energy, are: −475.429 98, [−475.441 74], −630.455 36, [−630.393 81], −713.205 17, [−713.209 89]. [b] Not computed. [c] Including diethyl ether bulk solvation effects at the SM5.42R/BPW91/6-31G* level.

decomplexation, so that ethereal solvation should not have a deleterious effect on addition/rearrangement selectivity.

Thermolysis of Alternative Fluorinated Oxiranes. The relatively high barrier predicted for the cracking of **6** may be a complication when other components of a given reaction mixture have thermal stability issues. As a result, it is of some interest to explore the reactivity of oxirane molecules having different functional groups that might be expected to additionally stabilize the carbonyl fragment produced by cracking, and thus potentially lower the barrier to cracking as well.

Table 1 presents barrier heights for four additional cracking reactions of three different oxiranes; structures are provided in Figure 4. As our intent is simply to qualitatively characterize energetic trends deriving from substitution, these calculations are carried out at the more economical BPW91/cc-pVDZ//HF/3-21G level. Calculations at this level give quite reasonable agreement with BPW91/cc-pVDZ for the difference in the cracking barriers associated with the two oxiranes, **3** and **6**, already discussed. Note, however, that this agreement must involve cancelation of various errors introduced by the lower level of theory used for geometry optimization. Poor transition-state structure geometries at the HF/3-21G level derive from the deficiency of single-determinant Hartree−Fock theory in describing unstabilized singlet carbene character present in the TS.[41,57] On the other hand, as noted in the Appendix, the transition state structures are rather floppy, so large geometric changes are less costly in an energetic sense than might otherwise be expected. In any case, we expect *qualitative* trends to be trustworthy at this level.

The case of 1-fluoro-1-(trifluoromethyl)oxirane (**8**), which can crack to give **4** and formaldehyde, can be regarded as the benchmark for an unstabilized carbonyl. This reaction has a barrier height of 69.5 kcal/mol and, as expected, a very late transition state. Replacement of both hydrogen atoms with fluorine atoms (i.e., creating **3**) lowers the barrier by 24.6 kcal/mol, suggesting that each fluorine atom stabilizes the incipient carbonyl in the transition state by about 12 kcal/mol relative to formaldehyde. The observation in carbenes that a trifluoromethyl group has roughly the same stabilizing power as a hydrogen atom[46] extends only partially to the incipient carbonyl fragment as well, since the barrier for cracking of **6** at this level is 5.5 kcal/mol lower than that for **8**—about half the amount expected from the single fluorine atom substituent if the trifluoromethyl group exerted no influence.

Replacing one fluorine atom in **6** with an hydroxyl group gives oxirane **9**. Trifluoroacetic acid and **4** would be the cracking products and the barrier is 2.9 kcal/mol lower than the cracking of **6**, consistent with the greater stability of a carboxylic acid compared to an acyl fluoride (**5**). Further replacement of the trifluoromethyl group at that center with another hydroxyl in 2-fluoro-1,1-dihydroxy-2-(trifluoromethyl)oxirane (**10**), so as to produce **4** and carbonic acid as the cracking products, reduces the absolute barrier height to only 32.9 kcal/mol.

However, the physical characteristics that make a substituent a good stabilizing group for the incipient carbonyl are unfortunately the same as those making it a good stabilizing group for an incipient carbene. Thus, the barrier for cracking **10** to give dihydroxycarbene and **2** is predicted to be 23.4 kcal/mol lower than the barrier for cracking to create carbonic acid and **4**. This is even larger than the difference found for the alternative cracking pathways of **3**, reflecting the still greater stability of singlet dihydroxycarbene[32,41,58−62] compared

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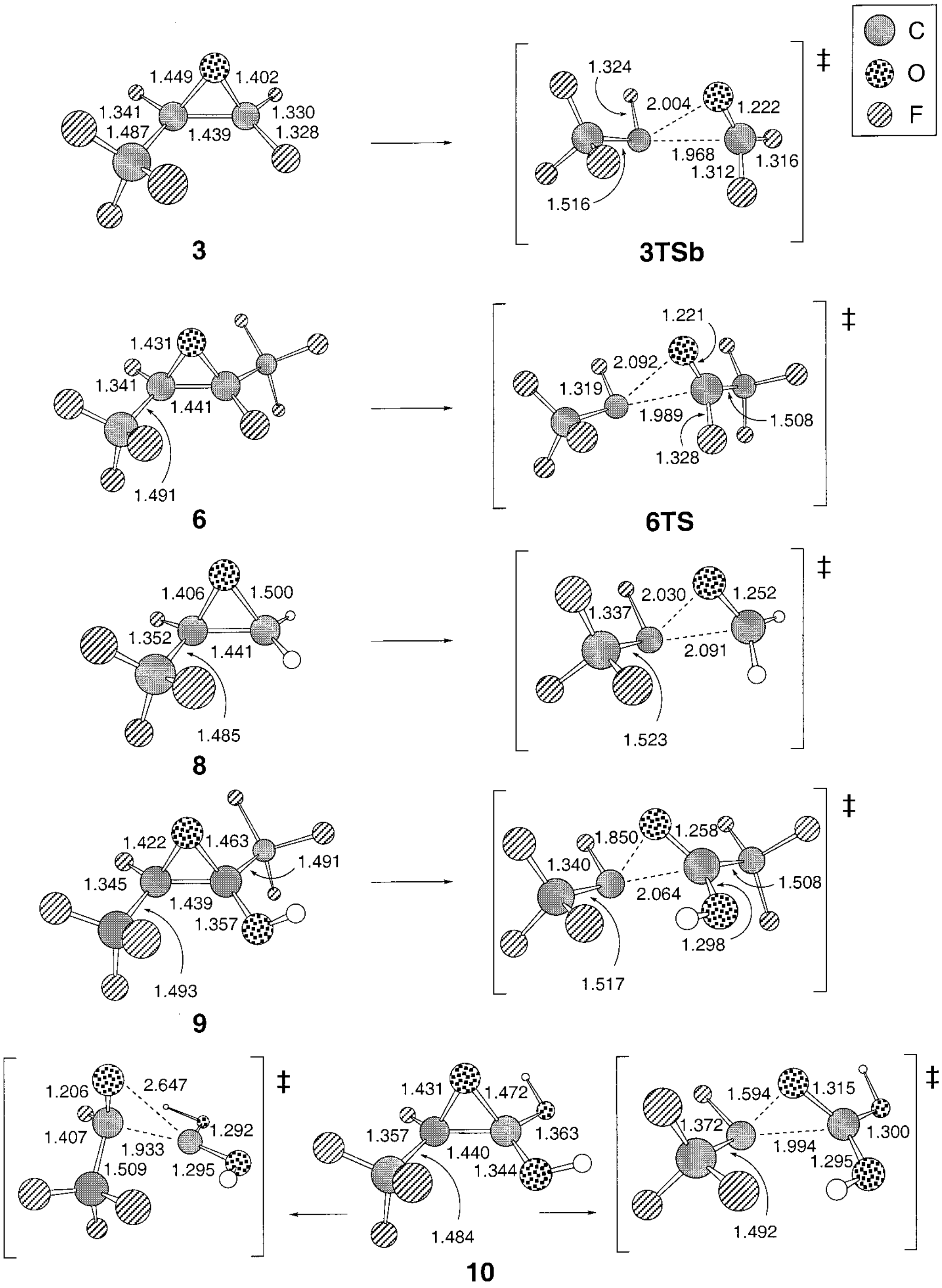
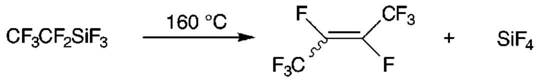


Figure 4. Optimized structures for various oxirane cracking stationary points at the RHF/3-21G level. Selected heavy-atom bond lengths (Å) are provided.

to **1**. This suggests that symmetrically substituted oxiranes will be required for the formation of relatively unstabilized fluoro(perfluoroalkyl)carbenes.

Tetrafluorosilane Extrusion. An alternative reaction that generates perfluoroalkylcarbenes under milder conditions than oxirane cracking involves extrusion of a fluorometalloid from the corresponding perfluoroalkylmetalloid. Although fluoroalkylmetal complexes based on Hg, Cd, and Sn have been examined experimentally,[9] we have limited our consideration here to perfluoro-1-silylethane. This substrate can extrude SiF_4 to produce **4**, whose intermediacy has been inferred from the observation of its dimerization product, perfluoro-2-butene.[63]



At the BPW91/cc-pVDZ level, extrusion is predicted to be barrierless and endoergic in a free energy sense by 33.9 kcal/mol,[64] which is about 18 kcal/mol lower in

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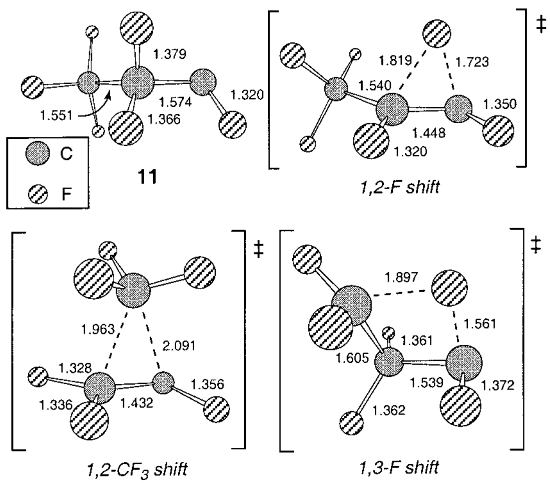

Figure 5. Optimized structures for stationary points associated with rearrangement of **11** at the BPW91/cc-pVDZ level. Selected heavy-atom bond lengths (Å) are provided.

energy than the barrier to crack **6**. The low energy of the asymptote (i.e., of the separated products) derives from the very strong Si−F bond formed in SiF_4. This asymptote may be compared to that for C−Si bond homolysis, which is endoergic in a free energy sense by 62.6 kcal/mol. Thus, concerted fragmentation is more favorable than C−Si bond homolysis by 28.7 kcal/mol.

In some sense, one may think of the net reaction using this substrate for cyclopropanation of a polymer as a carbene transfer. Addition across double bonds is more exoergic than insertion into very strong Si−F bonds, and this drives the transfer in the desired direction under conditions where fragmentation is kinetically significant. Such conditions would be expected to be milder than those required for cracking of **6**. Although synthetic considerations make oxiranes appear more attractive precursors than perfluoroalkylmetalloids, silane extrusion may be useful in instances where experimental conditions dictate lower temperatures be employed.

Rearrangements in Fluoro(perfluoroalkyl)carbenes. A final issue arises in the chemistry of (perfluoroalkyl)fluorocarbenes when the perfluoroalkyl substituent is larger than trifluoromethyl. In such instances, in addition to the 1,2-fluorine shifts already discussed, there is the potential either for perfluoroalkyl groups to undergo 1,2-shifts or for β-fluorine atoms to undergo 1,3-shifts. For the case of perfluoro-1-propanylidene (**11**), we have computed the transition state structures for all three possible rearrangements, and they are provided in Figure 5. The energetics of the rearrangements are summarized in Table 2.

The additional trifluoromethyl group has a very small impact on the 1,2-fluorine migration. The gas-phase 298 K free energy of activation for this process in **11** is 25.9 kcal/mol, which is only 1.0 kcal/mol higher than for the analogous rearrangement of **4**. The overall reaction to produce perfluoropropene is computed to be exoergic by 56.5 kcal/mol, which is 15.4 kcal/mol more exoergic than rearrangement of **4**. The relative insensitivity of the barrier height to reaction exoergicity is consistent with the very early transition states that are expected from the Hammond postulate.[43] In further accord with that postulate, the TS for the more exoergic 1,2-F shift of **11** *is* earlier than the analogous TS of **4**, as judged by the length of the newly forming C−F bond (0.046 Å less formed in TS of **11**) and of the breaking C−F bond (0.038 Å less broken in TS of **11**). On the other hand, the TS structures *do* appear to be fairly advanced in an absolute sense, suggesting that the Hammond postulate may not be entirely valid in this system. In fact, this same observation of a seemingly advanced TS structure was made for the rearrangement of vinylidene to acetylene some 20 years ago.[65] Subsequent work[66] rationalized this apparent paradox by considering the rearrangement to be the sum of two separate processes, hydrogen migration and π bond formation, and suggested that while each separately obeys the Hammond postulate, their sum does not. This analysis would be expected to generalize to most carbene rearrangements.

The other possible 1,2-shift, the 1,2-trifluoromethyl shift, is predicted to have a significantly lower barrier than the 1,2-fluorine shift. This process in **11** has a computed free energy of activation of 18.5 kcal/mol. Applying simple transition state theory again, the unimolecular rate constant for this rearrangement would be predicted to be slightly below 10^6 s^{-1} at 500 K, indicating that increased olefin concentrations may be required to maintain high conversion ratios for insertion vs rearrangement with **11**.

The last possible migration in **11**, the 1,3-fluorine shift, is predicted to have the highest free energy of activation of all at 36.4 kcal/mol. The relative magnitude of the activation free energy probably reflects in part the lower exoergicity associated with forming perfluorocyclopropane compared to perfluoropropene. In any case, this process would seem to be unimportant as a potentially unproductive side pathway.

Thus, considering the three possible rearrangements of **11**, the 1,2-trifluoromethyl shift is predicted to have the lowest barrier, the 1,2-fluorine shift has a higher barrier, and the 1,3-fluorine shift has the highest barrier of all. It is worth noting that this ordering of rearrangement barriers is substantially different than that found for hydrocarbon analogues. To compare, we can consider the predictions of Sulzbach et al.[67] for 2-butylidene and of Armstrong et al.[68] for 2,2-dimethyl-1-propenylidene. As summarized in Figure 6, the usual order of reactivity is that 1,2-H shifts have the lowest barriers, 1,3-H shifts have only slightly higher barriers, and 1,2-alkyl shifts have the highest barriers of all. (The differences exhibited between the two hydrocarbon systems for the 1,2-methyl and 1,3-H shifts are primarily manifestations of differences in reactant and product stabilities—the more-substituted carbene is more stable as a reactant, and pathways leading to more highly substituted alkenes have TS structures reflecting some of the lower energy associated with those species.)

The effect of fluorination is best rationalized by viewing these various rearrangements as insertion processes. The

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(64) Extrusion is endoergic in a potential energy sense by 47.7 kcal/mol. The absolute values (h) of E and G°_{298} for perfluorosilylethane at the BPW91/cc-pVDZ level are −1164.56685 and −1164.57303, respectively.

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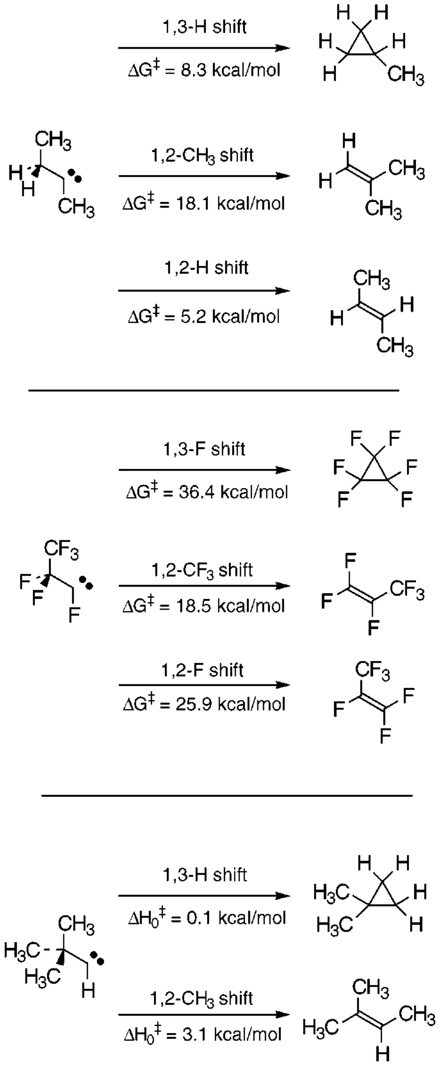

Figure 6. Barriers predicted for various carbene rearrangements. Barriers for 2-butylidene are 298 K free energies computed at the CCSD(T)/DZP level with BH&HLYP/DZP thermal contributions (ref 67). Barriers for 2,2-dimethyl-1-propanylidene are 0 K enthalpies computed at the QCISD(T)/6-31G*//MP2/6-31G* level (ref 68). Barriers for **11** are 298 K free energies computed at the BPW91/cc-pVDZ level (this work).

empty carbenic orbital inserts into a filled σ orbital, and the barrier height will be lowest when the orbitals involved have both good overlap *and* a small separation in energies.[69] Differences in reactivity, then, will be associated with differences in C−H vs C−F σ bond orbital energies or, for 1,2-alkyl migrations, with differences in F_nC-CF_n vs H_nC-CH_n σ bond orbital energies. In the former case, such differences would be expected to be very large, with the σ electrons being much less tightly held in the C−H bond than the C−F, and this is reflected in the much lower barrier heights for H migrations than for F migrations. [Note that experimentally H migrations will typically be further accelerated by tunneling contributions,[70−74] but here we are comparing simply barrier heights.] Orbital energies for C−C σ bonds, on the other hand, are less affected by substitution, and indeed the absolute barrier heights predicted for 1,2-alkyl migration in **11** and 2-butylidene are rather similar.

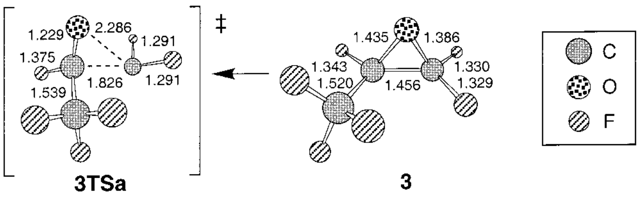

Figure 7. Optimized structures for stationary points **3** and **3TSa** at the MP2/cc-pVDZ level. Selected heavy-atom bond lengths (Å) are provided.

Conclusions

Thermal cracking of substituted oxiranes to generate perfluoroalkylcarbenes is expected to be generally extensible from the currently known technology for the generation of difluorocarbene. Such oxiranes will need to be designed in a symmetric fashion owing to the lower stability of (perfluoroalkyl)fluorocarbenes compared to difluorocarbene. Once generated, the carbenes are reasonably stable with respect to unimolecular rearrangement, so that high selectivity for reaction with olefins may be expected provided olefin concentrations are kept at sufficiently high levels. Of available rearrangement pathways, 1,2-perfluoroalkyl shifts are lowest in energy, 1,2-fluorine atom shifts are higher, and 1,3-fluorine atoms shifts are higher still; this ordering inversely reflects the relative orbital energies of the σ bonds broken in the respective migrations. In instances where the thermal conditions required for oxirane cracking are expected to be incompatible with other species in the reaction medium, extrusion of SiF_4 from perfluorosilylalkanes may be an attractive alternative for perfluorocarbene generation.

Appendix

One of us has previously found that DFT calculations using polarized double-ζ basis sets provide generally excellent agreement with geometries and singlet−triplet energy splittings for carbenes where high-quality gas-phase experimental data are available.[41] Other studies, often involving comparisons of theory to condensed-phase data, have also reported favorably on DFT as applied to carbenes.[37,46d,57,75−94] However, insofar as benchmarking of this level has been done neither for perfluorinated carbenes (other than **1**) nor for their epoxide cracking reactions, we did examine the quantitative utility of the BPW91/cc-pVDZ level in comparison with other levels of theory that experience suggests might be useful.

In particular, we compared DFT structures for **3** and **3TSa** to those computed at the MP2/cc-pVDZ level, i.e., taking account of electron correlation at the level of second-order many-body perturbation theory.[21] The MP2 structures are provided in Figure 7 and may be compared to the DFT structures in Figure 1. It is apparent that the MP2 level almost always predicts bond lengths for

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typical heavy-atom−heavy-atom bonds to be 0.010 to 0.015 Å shorter than those predicted at the DFT level. The error in this case appears to lie with an incomplete accounting for electron correlation (which usually leads to longer bonds) at the MP2 level rather than with any inadequacy in the DFT treatment. Thus if we consider carbonyl difluoride, for which the experimental C−F bond length is known to be 1.338 Å,[21] the DFT prediction is 1.337 Å and the MP2 prediction is 1.323 Å, i.e., the bond is predicted to be 0.015 Å too short at the MP2 level.

For the two forming/breaking bonds in **3TSa**, differences in bond lengths between the two levels of theory are considerably larger—about 0.15 Å for each. However, the potential energy surface is very flat in this region—comparing the predicted barrier height for cracking at the MP2 level using MP2 structures (42.0 kcal/mol) to the MP2 level using DFT structures (40.9 kcal/mol) one concludes that structural differences between MP2 and DFT are relatively unimportant from an energetic standpoint. Indeed, the 1.1 kcal/mol energy difference in the barrier heights is almost entirely (1.0 kcal/mol) attributable to differences in the structure of the *reactant*, **3**, not the transition state; despite the large geometric difference, the energy difference between the two **3TSa** structures at the MP2 level is only 0.1 kcal/mol.

Of course, the MP2 barrier (41−42 kcal/mol) is considerably higher than the predicted DFT barrier (35.3 kcal/mol). One may then question which level is more accurate, particularly since barrier heights often appear to be somewhat underestimated at the DFT level.[95] To evaluate this question further, we have performed coupled cluster calculations[96−99] including all single, double, and perturbatively estimated triple excitations with the same basis set (CCSD(T)/cc-pVDZ//BPW91/cc-pVDZ). In the absence of triple excitations, i.e., at the CCSD level, the predicted barrier is 40.5 kcal/mol, in good agreement with the MP2 level, which is not too surprising insofar as both levels consider only the effects of single and double excitations (although CCSD does so to infinite order). Inclusion of triples, however, drops the barrier to 37.7 kcal/mol, indicating the importance of higher-order correlation effects in lowering the transition state. The CCSD(T) level is in general more sensitive to basis-set incompleteness than the DFT level for such carbene properties as state energy splittings,[41,57] and our experience suggests that the remaining difference between the two for the barrier height discussed here is of a magnitude consistent with basis-set incompleteness being the remaining source of error. Further support for this contention is provided by the experimentally measured Arrhenius activation energy for this reaction of 36.3 kcal/mol.[45]

These benchmark calculations, then, suggest that the BPW91/cc-pVDZ level of theory should provide good quality structures and should further predict reaction energetics to within about 2 kcal/mol. Errors in reaction thermochemistries may be somewhat larger because of well-known deficiencies in the rigid-rotor harmonic-oscillator approximation used in the calculation of the vibrational frequencies.[21]

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