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# Homolysis of allyloxy(hydroxy)carbene. A density functional theory and *ab initio* study †

**Darren L. Reid and John Warkentin** *

*Department of Chemistry, McMaster University, Hamilton, ON, Canada L8S 4M1*

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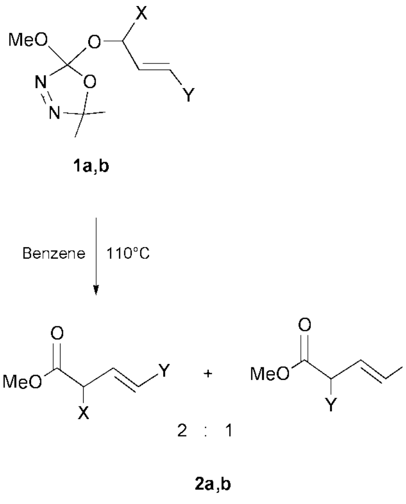
Warkentin and Venneri have shown that the bulk of the rearrangement products of allyloxy(methoxy)carbenes result from a homolysis–recoupling mechanism in contrast to the known cases of [2,3]sigmatropic rearrangements of analogous (bisheteroatom)carbenes (*J. Am. Chem. Soc.*, 1998, **120**, 11182). Herein, allyloxy(hydroxy)carbene is used as a model to investigate the fragmentations with density functional and Møller–Plesset calculations. [1,2]Migration, [2,3]sigmatropic rearrangement, β-scission from the triplet, and homolysis from the singlet state are all examined. Homolysis of singlet allyloxy(hydroxy)carbene is shown to be a viable pathway, and is best able to explain the experimental results.

## Introduction

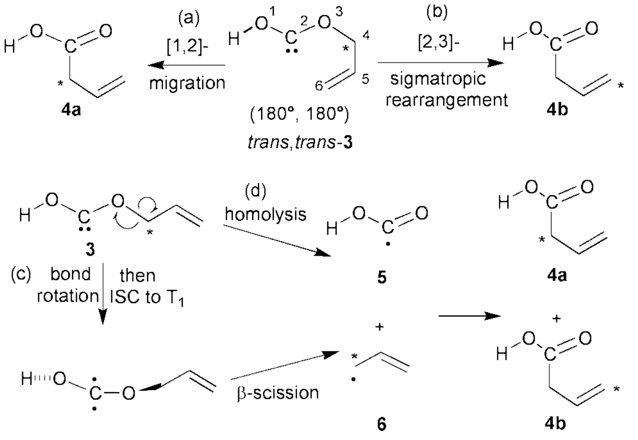
Venneri and Warkentin have recently reported that the oxadiazolines **1** undergo thermolysis in solution (110 °C, sealed tube) to the esters **2** [eqn. (1)].[1] The oxadiazolines afforded dioxycarbene intermediates, which could be trapped with *tert*-BuOH, but the esters arose from radicals (which could be trapped with TEMPO) either by mechanism c or d of Scheme 1. We now report computational work that identifies path d, the homolysis of a singlet ($S_0$) dioxycarbene, as a viable mechanism. This result is surprising in view of the known cases of [2,3]sigmatropic rearrangements of analogous (bisheteroatom)carbenes.[2] The thermal fragmentations are reminiscent of the radical mechanism accepted for the [1,2]Wittig rearrangement of deprotonated ethers.[3] In the case of an allyl ether, the [2,3]Wittig rearrangement is favoured.[2a,4] Wittig rearrangements have been the subject of a number of theoretical investigations but such studies are complicated by the uncertain role of the counterion.[5]



(1)

**a** = (X = Ph, Y = H); **b** = (X = H, Y = Ph)

Little theoretical consideration has been given to the homolysis of oxy- and dioxycarbenes. Computational work on the photochemical rearrangement of carbonyl compounds to oxycarbenes[6] indirectly explored a homolysis mechanism involving β-scission from the triplet ($T_1$) state of the oxycarbene. Borden *et al.* did consider the homolysis of the W-conformer of singlet ($S_0$) dihydroxycarbene (DHC) and found the H and COOH radicals to be 48 kcal mol$^{-1}$ (CISD/STO-3G) above the carbene (43 kcal mol$^{-1}$ at the CISD/DZP level).[7] These authors found an additional barrier of ~3 kcal mol$^{-1}$ between the carbene and the radicals that they considered to be too large and possibly not real. Recent results from our group at the (8,8)MRCI/cc-pVDZ//(8,8)CAS/cc-pVDZ level of theory predicted an additional barrier of 6.0 kcal mol$^{-1}$ for the homolysis of singlet *trans*-hydroxycarbene, with no such barrier for the *cis*-isomer.[8] It was shown that the change from the ground state carbene configuration to the radical pair configuration involves a substantial reorganization of the geometric and electronic structure for the *trans*-carbene, resulting in an additional barrier.



**Scheme 1**

In the present work four mechanisms (Scheme 1) for the formation of the esters [eqn. (1)] were investigated with the GAUSSIAN94, Revision E.2, system of programs,[9] using allyloxy(hydroxy)carbene (AHC) **3** as a model for allyloxy(methoxy)carbenes.

## Results and discussion

Electron correlation was included with the B3LYP density functional theory (DFT) hybrid method and the Møller–Plesset

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† Structural data are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b001033m

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**Table 1** Relative energies[a,b] ($\Delta E_T$) (kcal mol$^{-1}$) of constrained[c] $S_0$ and $T_1$ AHC conformers

| | | B3LYP/6-31+G(d) | | MP2(FC)/6-31+G(d) | |
|---|---|---|---|---|---|
| $\theta_1$/° | $\theta_2$/° | $S_0$ | $T_{1v}$[d] | $S_0$ | $T_{1v}$[d] |
| 0 | 0 | 11.7 | 84.0 | 12.9 | 87.0 |
| 0 | 90 | 19.5 | 71.5 | 20.9 | 75.5 |
| 0 | 180 | 0.5 | 75.6 | 0.9 | 77.8 |
| 90 (270) | 0 | 20.6 | 72.6 | 22.3 | 76.8 |
| 90 | 90 | 41.0 | 66.5 | 44.8 | 70.0 |
| 270 | 90 | 38.5 | 64.5 | 42.0 | 68.1 |
| 90 (270) | 180 | 17.2 | 68.1 | 18.3 | 72.3 |
| 180 | 0 | 2.5 | 74.6 | 2.5 | 78.1 |
| 180 | 90 | 17.6 | 64.7 | 18.9 | 69.4 |
| 180 | 180 | 0 | 72.0 | 0 | 75.5 |

[a] Total energy of (180°, 180°) conformer is −306.40109 hartree. [b] Minor errors may be expected here due to the conformational mobility of the allyl group. [c] $\theta_1$ and $\theta_2$ frozen; all other parameters optimized. [d] $T_{1v}$: vertical $T_1$ surface.

**Table 2** Energies, relative to *trans*,*trans*-AHC, in kcal mol$^{-1}$ for the stationary points

| | B3LYP/X[a] | | B3LYP/Z//B3LYP/X[a] | MP2(FC)/X[a] | |
|---|---|---|---|---|---|
| Isomer | $\Delta E_T$ | $\Delta E_T$ + ZPE | $\Delta E_T$ | $\Delta E_T$ | $\Delta E_T$ + ZPE |
| *trans*,*cis*-AHC | 2.5 | 2.4 | 2.7 | 2.4 | 2.5 |
| *cis*,*trans*-AHC | 0.5 | 0.1 | 0.7 | 0.9 | 0.5 |
| **TS1(a)** | 44.0 | 41.9 | 43.6 | 45.8 | 43.9 |
| **TS1(b)** | 42.8 | 40.8 | 42.5 | 44.6 | 42.5 |
| **TS2** | 17.3 | 15.6 | 16.6 | 18.4 | 16.8 |
| **TS3(a)** | 22.0 | 20.9 | 21.2 | 25.6 | 24.8 |
| **TS3(b)** | 22.9 | 20.9 | 21.8 | 26.0 | 24.9 |
| **TS4** | 15.1 | 14.3 | 14.7 | 16.6 | 15.7 |
| *trans*-**4** | −49.1 | −49.0 | −50.5 | −53.1 | −53.0 |
| *cis*-**4** | −55.2 | −54.9 | −55.6 | −59.8 | −59.5 |
| *trans*-**5** + **6** | 18.6 | 13.8 | 16.5 | 29.8 | 25.3 |
| *cis*-**5** + **6** | 20.5 | 15.5 | 18.4 | 31.7 | 27.0 |

[a] X and Z represent the 6-31+G(d) and 6-311++G(3df,2p) basis sets respectively. For *trans*,*trans*-AHC in hartrees; $\Delta E_T = -306.40109$, $\Delta E_T$ + ZPE = −306.30823 at the B3LYP/X level, $\Delta E_T = -305.47133$, $\Delta E_T$ + ZPE = −307.37828 at the MP2(FC)/X level and $\Delta E_T = -306.50772$ at the B3LYP/X//B3LYP/Z level.

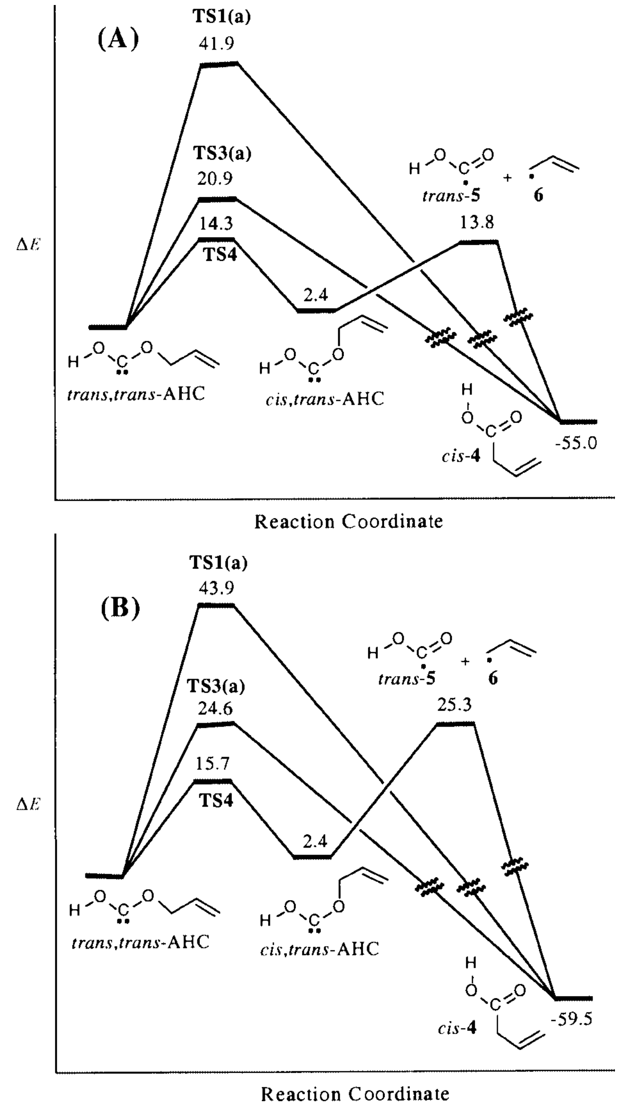

**Fig. 1** Schematic representation of the reaction coordinate (kcal mol$^{-1}$) for the rearrangements of AHC at the: (A) B3LYP/6-31+G(d) + ZPE level, (B) MP2(FC)/6-31+G(d) + ZPE level.

method with the correlation energy truncated at the second order (MP2). While Møller–Plesset methods have long been accepted in the carbene field as a reliable method for the inclusion of electron correlation energy, DFT methods have also gained widespread acceptance in recent years.[10] MP2 calculations were run with the frozen core approximation. Zero point energies were corrected using a scaling factor of 0.98 and 0.97 for the B3LYP and MP2 methods, respectively.[11] The triplet calculations were unrestricted and dissociation energies were calculated by optimizing the radicals individually as unrestricted doublets. All other calculations were restricted unless stated otherwise. For AHC, the 180° HOCO and OCOC dihedral angles ($\theta_1$, $\theta_2$) define the *trans*,*trans*-conformation (Scheme 1). Calculations on the conformers of AHC agree with those by Räsänen *et al.* for DHC in that the (180°, 180°) or *trans*,*trans*-conformer has the lowest energy at higher levels (Table 1).[12] Energies are therefore given relative to the fully optimized *trans*,*trans*-AHC (179.8°, 179.4° (B3LYP); 179.6°, 178.5° (MP2)) and the text refers to $\Delta E_T$ + ZPE at the B3LYP/6-31+G(d) or MP2(FC)/6-31+G(d) level unless stated otherwise (Table 2). Single point calculations, using the larger B3LYP/6-311++G(3df,2p) basis set on the B3LYP/6-31+G(d) stationary points, had only minor effects on $\Delta E_T$ (Table 2). Some key results for singlet AHC are summarized in Fig. 1, starting from its lowest energy conformation (*trans*,*trans*) and ending with the lowest energy conformation of the acid (*cis*-**4**). For convenience, the allyl substituent is drawn in the OCOC plane, although the lowest energy conformers have twisted COCC and OCCC dihedral angles. Minor differences imposed by other stable HOCO ($\theta_1$) conformations are presented in Table 2 and discussed below.

For *trans*,*trans*-AHC the lowest energy transition state for the concerted [1,2]migration (**TS1(a)**) (Scheme 1a) was 41.9 and 43.9 kcal mol$^{-1}$ above this conformer at the B3LYP and MP2 levels, respectively (Table 2, Fig. 1). However, the lowest energy transition state, (**TS1(b)**), for the [1,2]migration of *cis*,*trans*-AHC, was located at 40.8 (B3LYP) and 42.5 kcal mol$^{-1}$ (MP2). The *cis*,*trans*-AHC conformer lies only 0.1 (B3LYP) and 0.5 kcal mol$^{-1}$ (MP2) above the *trans*,*trans*-conformer, while the rotational barrier (**TS2**) for conversion of *trans*,*trans*-AHC to *cis*,*trans*-AHC is 15.6 (B3LYP) and 16.8 kcal mol$^{-1}$ (MP2). There have previously been a couple of theoretical investigations of [1,2]-alkyl rearrangements for oxycarbenes.[13,14] As might be expected, the [1,2]-allyl rearrangement barriers presented here for AHC are lower than the 60.2 kcal mol$^{-1}$ (PMP4/6-31G*//UHF/6-31G*) barrier for the [1,2]-$CF_3$ migration of trifluoromethoxy(hydroxy)carbene, although a direct comparison cannot be made.[13] The [1,2]-allyl migration was also found to occur out-of-plane (51.7° (B3LYP) and 53.8° (MP2),

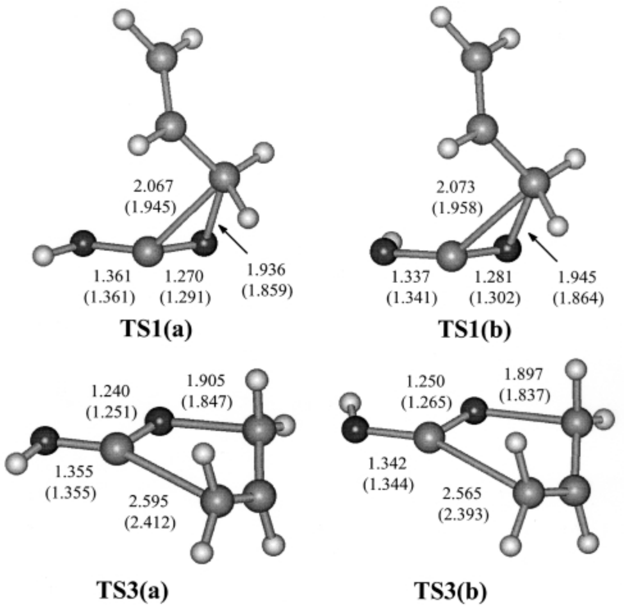

**Fig. 2** TS geometries for the [1,2]migration and [2,3]sigmatropic shift at the B3LYP/6-31+G(d) level showing the bond lengths (Å). The MP2(FC)/6-31+G(d) bond lengths (Å) are given in brackets.

for **TS1(a)**; 46.8° (B3LYP) and 52.5° (MP2) for **TS2(b)**) like the CF$_3$ migration in hydroxy(trifluoromethoxy)carbene (57.6°) and unlike the [1,2]-H migrations of DHC, which proceed in-plane (Fig. 2).[7,15] The reaction coordinate for the [1,2]-allyl migration of allyloxycarbene has also been analyzed by Iwamura *et al.*[14] Although they made no attempt to optimise a transition state, the barrier for the migration was estimated at 42.5 kcal mol$^{-1}$ at the MINDO/3 level of theory.

Iwamura *et al.* have also examined the reaction coordinate for the [2,3]sigmatropic rearrangement of allyloxycarbene at the MINDO/3 level of theory. The barrier for rearrangement was estimated to be 31.5 kcal mol$^{-1}$. The transition states reported here (**TS3(a)** and **TS3(b)**) for the [2,3]sigmatropic rearrangement (Scheme 1b) resemble the Rautenstrauch model for the [2,3]Wittig rearrangement in that the C5 is out of the plane of the 5-membered transition state (Fig. 2).[5a,d,e] **TS3(a)** and **TS3(b)** are early, which could indicate the presence of an intermediate on the reaction coordinates, but none was found with an intrinsic reaction coordinate calculation at the RB3LYP/6-31+G(d) level for the *trans*,*trans*-AHC reaction coordinate. These early transition states are consistent with the previous results for allyloxycarbene,[14] and are reasonable for exothermic reactions requiring relatively small activation energies, in accordance with the Hammond postulate.[16]

**TS3(a)** for the rearrangement of *trans*,*trans*-AHC was found to lie 20.9 (B3LYP) and 24.8 kcal mol$^{-1}$ (MP2) above the ground state, while **TS3(b)** for the migration in *cis*,*trans*-AHC was found to lie 21.0 (B3LYP) and 25.0 kcal mol$^{-1}$ (MP2) above *trans*,*trans*-AHC. Coincidentally the B3LYP values of $\Delta E$ + ZPE for **TS3(a)** and **TS3(b)** are identical, while **TS3(a)** is slightly lower in energy at the MP2 level of theory. These barriers for the [2,3]sigmatropic rearrangement are roughly half that of the [1,2]-allyl migration (Table 2, Fig. 1). This result is consistent with the antiaromatic nature of a partially-in-plane, four-electron transition state of the [1,2]migration, as compared to the allowed six-electron transition state of the [2,3]-sigmatropic rearrangement.[7,14,17] Clearly, the [2,3]sigmatropic shift, which is known for other (bisheteroatom)carbenes,[2] should be highly favoured over the [1,2]migration. Thus the observed product ratios[1] [eqn. (1)] cannot be explained in terms of a competition between these two rearrangements.

Homolysis of dioxycarbenes to give radicals by means of a β-scission from T$_1$ (Scheme 1c) requires that this state be well populated. The experimental results[1] indicate that most of the apparent rearrangement products **2** come from a radical path, requiring a small S$_0$–T$_1$ gap if the radicals came from the triplet carbene. The potential energy surfaces were initially mapped out at the HF/3-21G level with the (0°, 180°), (90°, 180°), (180°, 180°) and (270°, 180°) starting geometries, from which, with $\theta_1$ frozen, $\theta_2$ was rotated through to 0° in 10° steps as the geometry was optimized at every point for the S$_0$ surface. The vertical triplet surfaces (T$_{1v}$) were calculated at the S$_0$ geometries. Qualitatively, the HF/3-21G results mirror those for DHC in that minima on the S$_0$ surface correspond to maxima on the triplet surface and *vice versa*.[12,18] At this level of theory, the $\theta_1 = 90°$ and the $\theta_1 = 270°$ S$_0$ and T$_{1v}$ surfaces enter overlapping regions that move apart at the higher levels until the $\theta_1 = 90°$ and the $\theta_1 = 270°$ surfaces have S$_0$–T$_{1v}$ gaps of −25.5 and −25.9 kcal mol$^{-1}$ (B3LYP) (Fig. 3, Table 1) and −25.3 and −26.1 kcal mol$^{-1}$ (MP2) (Table 1), in excellent agreement with previous results for DHC[12,15c] and dimethoxycarbene.[19] The (90°, 90°) and (270°, 90°) conformers are, more or less, maxima that lie at 41.0 and 38.5 kcal mol$^{-1}$ (B3LYP) (Fig. 1) or 44.8 mol$^{-1}$ and 42.0 kcal mol$^{-1}$ at the MP2 level, above the lowest energy singlet (Table 1). It seems unreasonable then to suggest that the triplet state could be the radical source.

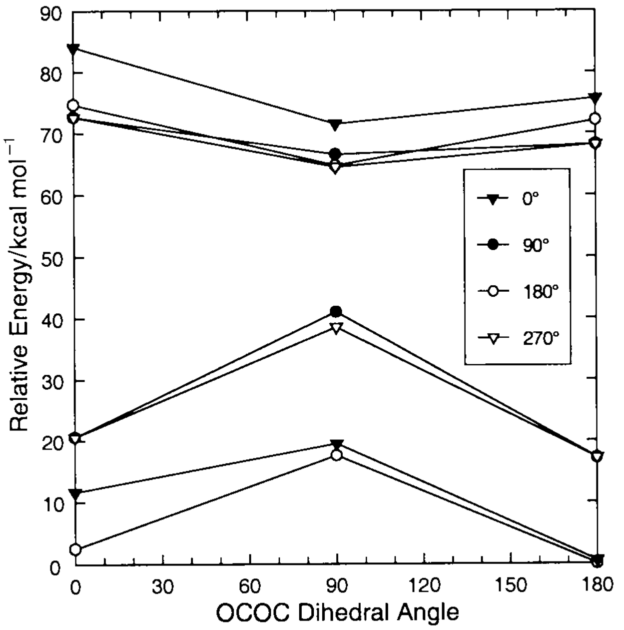

**Fig. 3** Energy diagram showing the singlet (S$_0$) and vertical triplet (T$_{1v}$) curves at the B3LYP/6-31+G(d) level, with $\theta_1$ (HOCO dihedral angle) frozen at 0, 90, 180 and 270°, rotating about $\theta_2$ (OCOC dihedral angle).

Fragmentation from the open shell singlet (S$_1$) can also be ruled out, since a singlet state possessing two half-filled orbitals is always of higher energy than the triplet state of the same electron orbital configuration.[20] This stabilization of a triplet state relative to a singlet state is due to the exchange correlation.[20b] Moss *et al.* have calculated that the HOMO→LUMO ($\sigma^2 \rightarrow \sigma^1 p^1$) excitation, to give the open-shell singlet for *cis*,*trans*- and *trans*,*trans*-dimethoxycarbene, costs 109 and 104 kcal mol$^{-1}$ at the CIS/INDO/S//6-31G(d) level of theory.[19] They found that this calculated gap corresponded to an observed absorption at 255 nm (112 kcal mol$^{-1}$).[19] At the request of a referee, the S$_0$–S$_1$ gap was calculated for the extended chain conformer of AHC, constrained to CS symmetry. This conformer was 2.2 and 3.0 kcal mol$^{-1}$ higher in energy than the lowest energy unconstrained AHC conformer at the B3LYP and MP2 levels of theory respectively, without ZPE. By using the Guess=Alter command, the vertical S$_0$–S$_1$ gap corresponding to the $\sigma^2 \rightarrow \sigma^1 p^1$ excitation of the symmetric AHC was found to be −83.3 and −112.5 kcal mol$^{-1}$ at the UB3LYP/

6-31+G(d)//RB3LYP/6-31+G(d) and PMP2/6-31+G(d)//RMP2/6-31+G(d) levels of theory. The spin projected Møller–Plesset (PMP2) values were used due to significant spin contamination of the excited singlet state.[21] The PMP2 result also appears to be a more reasonable value for the $S_0$–$S_1$ gap of AHC than the B3LYP result when compared to the experimental value for a similar dioxycarbene, dimethoxycarbene (255 nm, 112 kcal $mol^{-1}$).[19]

Previous work has shown that there could be a transition state associated with the homolysis of oxy- and dioxycarbenes when the leaving group is *syn* to the carbene lone pair, as it is in *trans*,*trans*-AHC.[7,8] However, results with hydroxycarbene suggest that a barrier should not be expected when the leaving group is *anti* to the carbene lone pair as in *trans*,*cis*-AHC.[8] Attempts to model these homolytic reactions at the QCISD levels of theory proved to be unsuccessful, and complete active space (CAS) calculations appear to provide the minimum level of electron correlation necessary. Unfortunately, the large active spaces required prohibit the use of these calculations for allyloxy(hydroxy)carbene. It is a simple matter, however, to calculate the dissociation energy of the carbene to radicals by calculating each of the radicals individually.[22] Large differences were observed for the B3LYP and MP2 results. The radicals (*trans*-**5** + **6**) were found to be 68.7 kcal $mol^{-1}$ (73.8 kcal $mol^{-1}$ without ZPE) above the lowest energy conformer of the carboxylic acid (*cis*-**4**) at the B3LYP level and 84.8 kcal $mol^{-1}$ (89.6 kcal $mol^{-1}$ without ZPE) at the MP2 level (Table 2, Fig. 1). The B3LYP results are in better agreement with the experimental[23] $\Delta H_f°$ of $75 \pm 1$ kcal $mol^{-1}$, consistent with those of previous workers, who have found that the DFT results give more reliable radical heats of formation than MP2 calculations.[22] The sum of the energies of the radicals, *trans*-**5** + **6**, was found to lie 11.4 kcal $mol^{-1}$ above *trans*,*cis*-AHC using DFT and 22.8 kcal $mol^{-1}$ using MP2 (Table 2, Fig. 1). The fully optimized *trans*,*cis*-AHC conformer lies 2.4 kcal $mol^{-1}$ above the *trans*,*trans*-AHC conformer, while the barrier for rotation to *trans*,*cis*-AHC through **TS4** (182.5°, 92.0° and 182.0°, 92.3°) is 14.3 and 15.7 kcal $mol^{-1}$ at the DFT and MP2 levels, respectively (Table 2, Fig. 1). It can be seen from Table 2 that the [2,3]sigmatropic rearrangement (**TS3(a)** and **TS3(b)**) has an activation energy that is either higher than, or about equal to, that of the homolysis. We propose that at 110 °C (the temperature for the reactions in eqn. (1)) radical formation from the singlet *trans*,*cis*-conformer should be the dominant pathway due to entropic effects (Scheme 1d). This expectation is in keeping with the known effects of temperature on Wittig rearrangements.[4*a*,24,25] The observed regiochemistry [eqn. (1)] may arise from solvent cage effects similar to those used to explain the high retention of stereochemistry also found for [1,2]Wittig rearrangements.[3]

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## References

1 P. C. Venneri and J. Warkentin, *J. Am. Chem. Soc.*, 1998, **120**, 11182.
2 (*a*) R. W. Hoffmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1979, **18**, 563; (*b*) J. E. Baldwin and J. A. Walker, *J. Chem. Soc.*, *Chem. Commun.*, 1972, 354; (*c*) T. Nakai and K. Mikami, *Chem. Lett.*, 1978, 1243; (*d*) T. Nakai and K. Mikami, *Chem. Lett.*, 1979, 1081.
3 K. Tomooka, H. Yamamoto and T. Nakai, *Liebigs Ann.*/*Recl.*, 1997, 1275.
4 (*a*) T. Nakai and K. Mikami, *Chem. Rev.*, 1986, **86**, 885; (*b*) R. Brückner, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Flemming, Pergamon Press, London, 1991, vol. 6, p. 873.
5 (*a*) T. Okajima and Y. Fukazawa, *Nippon Kagaku Kaishi*, 1999, 97 (*Chem. Abstr.*, 1999, **130**, 282090f); (*b*) J. C. Sheldon, M. S. Taylor, J. H. Bowie, S, Dua, C. S. Brian Chia and P. C. H. Eichinger, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 333; (*c*) P. Antoniotti and G. Tonachini, *J. Org. Chem.*, 1998, **63**, 9756; (*d*) T. Okajima, *Nippon Kagaku Kaishi*, 1997, 529 (*Chem. Abstr.*, 1997, **127**, 161403q); (*e*) T. Okajima and Y. Fukazawa, *Chem. Lett.*, 1997, 81 and references therein; (*f*) P. Antoniotti, C. Canepa and G. Tonachini, *Trends Org. Chem.*, 1995, **5**, 189; (*g*) P. Antoniotti and G. Tonachini, *J. Org. Chem.*, 1993, **58**, 3622; (*h*) C. K. Kim, B.-S. Lee and I. Lee, *J. Phys. Org. Chem.*, 1992, **5**, 812; (*i*) C. K. Kim, I. Lee, H. W. Lee and B.-S. Lee, *Bull. Korean Chem. Soc.*, 1991, **12**, 678.
6 (*a*) J. A. Altmann, I. G. Csizmadia, K. Yates and P. Yates, *J. Chem. Phys.*, 1977, **66**, 298; (*b*) J. A. Altmann, I. G. Csizmadia, M. A. Robb, K. Yates and P. Yates, *J. Am. Chem. Soc.*, 1978, **78**, 1653.
7 D. Feller, W. T. Borden and E. R. Davidson, *J. Comput. Chem.*, 1980, **1**, 158.
8 D. L. Reid, J. Hernández-Trujillo and J. Warkentin, *J. Phys. Chem.*, *A.*, 2000, **104**, 3395.
9 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *GAUSSIAN94*, *Revision E. 2*, Gaussian, Inc., Pittsburgh, PA, 1995.
10 (*a*) F. Mendez and M. A. Garcia-Garibay, *J. Org. Chem.*, 1999, **64**, 7061; (*b*) A. Nicolaides, T. Nakayama, K. Yamazaki, H. Tomioka, S. Koseki, L. L. Stracener and R. J. MaMahon, *J. Am. Chem. Soc.*, 1999, **121**, 10563; (*c*) E. Kohl, T. Ströter, C. Siedschlag, K. Polborn and G. Szeimies, *Eur. J. Org. Chem.*, 1999, 3057.
11 (*a*) A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502; (*b*) M. W. Wong, *Chem. Phys. Lett.*, 1996, **256**, 391.
12 M. Räsänen, T. Raaska, H. Kunttu and J. Murto, *J. Mol. Struct.* (*THEOCHEM*), 1990, **208**, 79.
13 J. S. Francisco, *J. Chem. Soc.*, *Faraday Trans.*, 1992, **88**, 3521.
14 H. Iwamura, M. Iwai and H. Kihara, *Chem. Lett.*, 1977, 881.
15 (*a*) J. D. Goddard, Y. Yamaguchi and H. F. Schaefer III, *J. Chem. Phys.*, 1992, **96**, 1158; (*b*) J. S. Francisco, *J. Chem. Phys.*, 1992, **96**, 1167; (*c*) R. L. Redington, C. W. Bock and B. Aboab, *J. Mol. Struct.*, 1990, **224**, 89.
16 G. S. Hammond, *J. Am. Chem. Soc.*, 1955, **77**, 334.
17 R. Hoffmann and R. B. Woodward, *Angew. Chem.*, *Int. Ed. Engl.*, 1969, **8**, 781.
18 (*a*) D. Feller, W. T. Borden and E. R. Davidson, *J. Chem. Phys.*, 1979, **71**, 4987; (*b*) D. Feller, W. T. Borden and E. R. Davidson, *Chem. Phys. Lett.*, 1980, **71**, 22.
19 R. A. Moss, M. Włostowski, S. Shen, K. Krogh-Jespersen and A. Matro, *J. Am. Chem. Soc.*, 1988, **110**, 4443.
20 (*a*) N. J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Co., Inc., London, 1978; (*b*) A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry*, McGraw-Hill Publishing Co., Toronto, 1982.
21 H. B. Schlegel, *J. Phys. Chem.*, 1988, **92**, 3075.
22 B. S. Jursic, *Int. J. Quantum Chem.*, 1997, **62**, 291 and references therein.
23 (*a*) S. W. Benson, *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, John Wiley & Sons, Inc., New York, 1976; (*b*) S. W. Benson and H. E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions*, National Bureau of Standards, NSRDS-NBS 21, USA, 1970.
24 V. Rautenstrauch, *J. Chem. Soc.*, *Chem Commun.*, 1970, 4.
25 J. E. Baldwin, J. DeBernardis and J. E. Partick, *Tetrahedron Lett.*, 1970, 353.