JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Intermolecular Reactions of a Foiled Carbene with Carbonyl Compounds: The Effects of Trishomocyclopropyl Stabilization

Ingrid Malene Apeland,[†] Murray G. Rosenberg,[§] Vladimir B. Arion,[‡] Hanspeter Kählig,[†] and Udo H. Brinker*[,†,§]

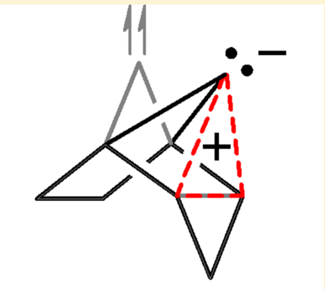
[†]Institute of Organic Chemistry, University of Vienna, Währinger Strasse 38, A-1090 Vienna, Austria

[§]Department of Chemistry, The State University of New York at Binghamton, P.O. Box 6000, Binghamton, New York 13902-6000, United States

[‡]Institute of Inorganic Chemistry, University of Vienna, Währinger Strasse 42, A-1090 Vienna, Austria

Supporting Information

ABSTRACT: *endo*-Tricyclo[3.2.1.0^{2,4}]oct-8-ylidene is a foiled carbene reaction intermediate. It was generated by thermolyzing Δ^3-1,3,4-oxadiazoline precursors dissolved in benzaldehyde and acetophenone. The products appear to stem from direct insertion of the carbene's divalent C atom into the α-bonds of the carbonyl compounds; however, this is only superficial. The strict stereochemistry observed is due to the topologies of the reaction intermediates of the proposed two-step mechanism. Bimolecular nucleophilic addition generates bent 1,3-zwitterions. The neutral reaction intermediates undergo pinacolic rearrangements to form the observed adducts. Product ratios reflect the migratory aptitudes of the carbonyl compounds' α-substituents. The carbene reaction was modeled using DFT. The singlet carbene's bicoordinate C atom bends 31° toward the *endo*-fused cyclopropane bond, elongating it to r = 1.69 Å. The resulting trishomocyclopropyl HOMO{−1} is a three-center two-electron bond responsible for the electron-deficient carbene's nucleophilicity. Its calculated properties are consistent with this assertion: (1) singlet−triplet (ΔE_{S-T}) energy gap of −25 kcal/mol, (2) gas-phase proton affinity (PA) value of 272 kcal/mol, (3) hard and soft acid and base (HSAB) ΔN value of −0.2 in its initial reaction with the carbonyl compounds, and (4) negative frontier orbital interaction values $\Delta\Delta E$(PhC(O)H) = −4.38 eV and $\Delta\Delta E$(PhC(O)Me) = −3.97 eV.


endo-Tricyclo[3.2.1.0^{2,4}]oct-8-ylidene

Singlet (:) *vs.* Triplet (↑↑) Structure

INTRODUCTION

The formation of three-membered rings by cycloaddition of singlet carbenes and multiple bonds can occur through a pericyclic transition state (TS).[1] The Woodward−Hoffmann selection rules[2] for a thermally allowed 4q (q = 1) cheletropic reaction[3,4] require the unsaturated compound to participate suprafacially and the carbene antarafacially (i.e., [$_{\pi}2_s$+$_{\omega}2_a$]), as depicted in Figure 1. A nonlinear p-approach of the carbene in an unsymmetric non-least-motion pathway mitigates steric repulsion between the molecules.[5] Neutral carbenes feature a divalent C atom.[6−14] The tetravalency of the C atom,[15] which is the basis of organic chemistry,[16] is restored when the hypovalent C atom obtains a Lewis octet. The electron-deficient carbene achieves this by reacting intra- or intermolecularly. Some carbenes rearrange to stable constitutional isomers or they add to solvent and/or solute molecules. Carbene reaction intermediates usually have short lifetimes, and their irreversible reactions are exothermic due to their high internal energies. Strategies to stabilize these reactive molecules have been pursued and have led to the development of "bottleable" carbenes.[17] Carbenes react according to their ground electronic-state spin multiplicity. Those with open-shell T_0(n,p) states behave as *gem*-biradicals, whereas those with closed-shell S_0(n,p) states often undergo polar reactions. Singlet carbenes are amphoteric and can act as Lewis acids or bases, but the majority of known carbenes behave as electrophiles. This report chronicles a nucleophilic carbene and its reactions with carbonyl compounds.

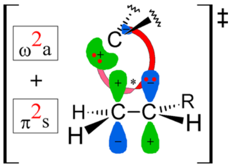


Figure 1. Cheletropic reaction of a singlet carbene and terminal alkene yielding a substituted cyclopropane. The Möbius (*) pericyclic TS has 4 electrons. Thus, it is allowed thermally.

"Foiled reaction" carbenes were conceived as an approach toward stabilizing the closed-shell S_1(n,p) state of a carbene to the point that it would supersede the T_0(n,p) state, thus becoming the ground electronic state.[18−20] Computational chemistry is an indispensable method to study short-lived

Special Issue: 50 Years and Counting: The Woodward-Hoffmann Rules in the 21st Century

Received: August 25, 2015
Published: October 8, 2015

ACS Publications © 2015 American Chemical Society

DOI: 10.1021/acs.joc.5b01988
J. Org. Chem. 2015, 80, 11877−11887

reaction intermediates.[21] It has provided insight into the nature of foiled carbenes,[22−24] such as *endo*-tricyclo[3.2.1.0^{2,4}]oct-8-ylidene (**1**) (Figure 2a)[25−28] and bicyclo[2.2.1]hept-2-en-7-ylidene (**2**) (Figure 2b).[29,30] Intramolecular carbene cycloaddition is foiled because the product would be greatly strained by its inverted C atom.[31] Instead, an in-between structure[18] is adopted. The C1−C7−C4 bridge of carbene **2** is predicted to tilt toward the C−C double bond, thus allowing the bicoordinate C atom to interact with it.[23] A delocalized three-center two-electron bond is formed from a triangular array of three basis set p-orbitals. The bishomocyclopropenyl ring stabilizes the hypovalent C atom of **2**, making it homoaromatic.[32,33] A similar situation exists in carbene **1** (Figure 2a).[25] It is a homologue of carbene **2**, wherein the vinylene group of **2** has been replaced by a fused endocyclic cyclopropane (see **1** in Scheme 1b) but not an exocyclic one (see *iso*-**1** in Scheme 1a). Indeed, the C2−C4 bent σ/π-bond of **1** mimics the C2−C3 π-bond of **2** because a "...cyclopropane ring more closely resembles the C═C bond than [a] cyclobutane ring"[34] and a "... cyclopropane ring may replace a π bond in the framework system for a sigmatropic change."[3] Thus, a delocalized three-center two-electron bond is formed in carbene **1** as well. The trishomocyclopropyl ring stabilizes the hypovalent C atom of **1**, making it homoaromatic.[32,33] The optimal structure of carbene **1** and its key MOs were computed using DFT and are shown in Figure 3.

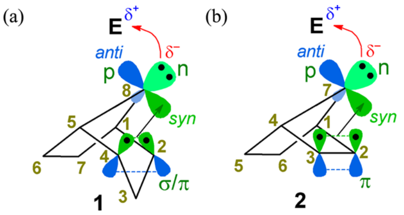
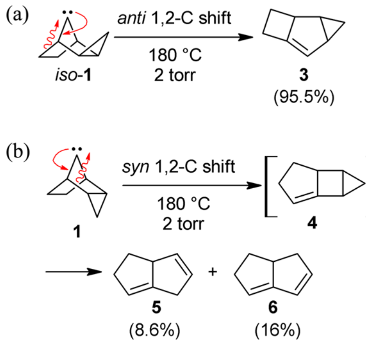


Figure 2. Homoaromaticity within foiled carbenes (a) *endo*-tricyclo[3.2.1.0^{2,4}]oct-8-ylidene (**1**) and (b) bicyclo[2.2.1]hept-2-en-7-ylidene (**2**), which differ only by an extra CH_2 group in **1** (i.e., C3), that is responsible for their bent geometries, singlet ground electronic states, nucleophilicities toward electrophiles **E**, and diastereoselectivities.

Scheme 1. Intramolecular Reactions of Gaseous Tricyclo[3.2.1.0^{2,4}]oct-8-ylidenes[a]



[a] cf. refs 40−42.

Intramolecular cycloaddition within **1** is foiled because [3.4.3.5]fenestrane is too strained.[35] Even trace amounts of 1,3-CH insertion are observed in **2**[30,36] but not in **1**. A bridgehead alkene arising from 1,2-H shift within **1** is also precluded[37−39] due to orbital misalignment. In contrast, fused bicyclic alkenes **5** and **6** are reported to stem from gaseous carbene **1**,[40−42] likely via *syn* 1,2-C shift (Scheme 1b). However, they are not formed in the condensed phase. Rapid bimolecular reactions prevail (e.g., solvolysis and ketazine formation).[25] The carbene−carbene rearrangement of **1** to tricyclo[3.3.0.0^{2,8}]oct-4-ylidene (**7**) has been reported (Scheme 2).[25,43−45] Intermolecular proton transfer within protic solvents has been proposed (Scheme 2).[44] Evidence of carbene **7** comes from its solvolysis products and the formation of isomers **8** and **9**.

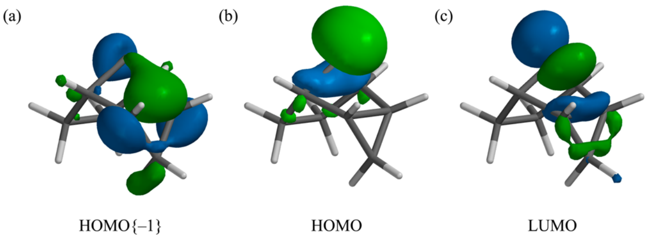
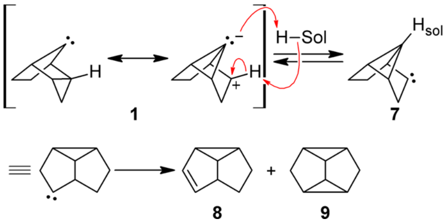


Figure 3. Bent carbene **1** features (a) a three-center two-electron bond (i.e., trishomocyclopropyl MO) derived from a triangular array of three basis p-orbitals (see Figure 2a), (b) a reactive lone pair of electrons (i.e., n-orbital), and (c) a virtual p-orbital (surfaces shown with a 0.07 isovalue computed using the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) theoretical model).

Scheme 2. Isomerization of Carbene 1 to Carbene 7 in Protic Solvent[a]



[a] See ref 44.

The intermolecular reactivities and stereoselectivities of foiled carbenes can be compared with the original predictions.[18] The *anti* face of carbene **2** is more exposed to oncoming reagents as a consequence of its bent geometry (Figure 2b). Thus, for example, the cyclopropanation of 2-methylpropene by **2** was envisioned to be stereoselective due to mutual orientations determined by steric factors.[18] In addition, carbene **2** was expected to initiate a nucleophilic reaction with R−X compounds to yield the *anti*-X configurational isomers.[18] However, a *syn*-Br product was isolated by reacting two *gem*-dibromo precursors with MeLi.[29,46,47] The results indicate that a carbenoid rather than a free carbene is involved. In a related case, **1** was generated from bicyclo[5.1.0]oct-3-en-8-ylidene via a homologous Skattebøl rearrangement.[45] Again, carbenoid chemistry is suspected because the product had a *syn*-Br configuration. More definitive studies involving the intermolecular reactions of foiled carbenes with alkenes[25,48−50] and alcohols[25,51,52] indicate that they undoubtedly exhibit nucleophilic behavior.[53]

Carbene nucleophilicity is achieved when an adjacent π-donor atom infuses electron density into the bicoordinate C atom's p-orbital.[54] An ylide results if the effect is large. For example, stable nucleophilic carbenes are formed by flanking a divalent C atom with two N atoms.[17,55−63] The reactivity of such carbenes is quite unlike that of more traditional electrophilic carbenes.[53] For example, deprotonation of thiazolium ions[64,65] with Et_3N generates an ylide that catalyzes acyloin condensations of aldehydes.[66] In the classic benzoin condensation,[67] the CN^- anion is used catalytically to dimerize PhC(O)H.[68−70] Foiled carbenes **1** and **2** are special because they are stabilized by noncontiguous electron-pair donors: a σ/π-bond and a π-bond, respectively (Figure 2). Each was determined from DFT calculations to be stabilized by ∼14 kcal/mol.[27]

The cycloaddition of carbene **1** and PhC(O)R [R = (a) H, (b) Me] via pericyclic TS was considered, but the necessary back-bonding by the O atom was deemed unavailable. Its n-orbital is orthogonal to the p-orbital of **1**; the almost-degenerate π_3 and π_4 MOs lie beneath the HOMO and are concentrated in the benzene ring and not in the CO bond. Therefore, direct Ad_N2 of PhC(O)R by **1** was examined. The n-orbital of a nonylidic nucleophilic carbene should initiate such an elementary step with just the C atom of carbonyl compounds RC(O)R′.[71−73] Indeed, the nucleophilicity of foiled carbenes is evident in the deprotonation of protic solvents.[61,74,75] By this manner, carbenes **1**[44] and **7**[25,44] formally insert into the O−H bond of MeOH. Even the active-methylene compound $(CN)_2CH_2$ yields the formal C−H insertion product of a foiled carbene.[76] The protonation was examined using the B3LYP/6-31G(d) theoretical model.[76] The initial TS leads to a tight ion-pair that recombines. Of course, foiled carbenes act as electrophiles in the presence of stronger nucleophiles, such as amine bases.[25] Such ambiphilicity has been shown in cycloadditions with various alkenes because carbene philicity is substrate-dependent.[53,77−79]

Intramolecular reactions of a divalent C atom and carbonyl group within an electrophilic carbene are well documented.[80−90] There are fewer examples of the intermolecular variant.[91−96] Still, less is known about the reactions of carbonyl compounds with nucleophilic carbenes.[71−73] Although carbonyl compounds are themselves amphoteric, they should react as electrophiles with nucleophilic carbenes.[53,54,97] The present study is the first to delve into the intermolecular reactions of a foiled carbene with carbonyl compounds; thus, computational chemistry was used to rationalize the experimental results obtained from carbene **1**.

■ RESULTS AND DISCUSSION

Δ^3-1,3,4-Oxadiazolines are popular and versatile sources of free carbenes that can be liberated by either photolysis or thermolysis.[71−73,98−115] The diastereomeric precursors *r*-**10** and *s*-**10** were used separately herein to generate carbene **1** (Figure 4). They were dissolved in either PhC(O)H or PhC(O)Me and heated to T = 165 °C until fully decomposed (Scheme 3).[25]

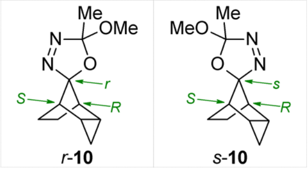
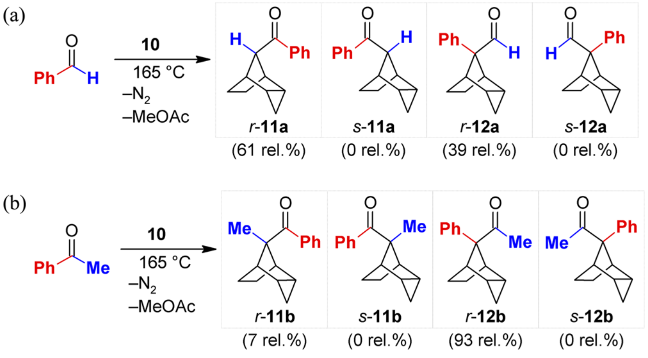


Figure 4. Δ^3-1,3,4-Oxadiazolines *r*-**10** and *s*-**10** were used as precursors for the thermolytic generation of carbene **1**.

Scheme 3. Intermolecular Addition of Carbene 1 and Carbonyl Compounds PhC(O)R Yields Constitutional Isomers 11 and 12 with Complete Stereocontrol[a]



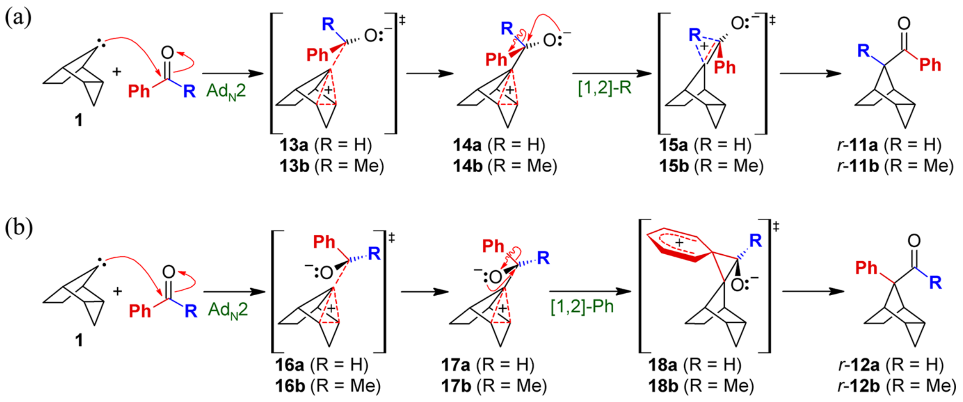
[a] R = (a) H or (b) Me.

Phenyl{*rac*-(1*R*,2*R*,4*S*,5*S*,8*r*)-tricyclo[3.2.1.0^{2,4}]oct-8-yl}-methanone (*r*-**11a**; Scheme 3a) was formed after individual thermolyses of the carbene **1** precursors *r*-**10** and *s*-**10** (Figure 4) in neat PhC(O)H. The major product was isolated in 53% yield from *r*-**10** and 43% yield from *s*-**10**. Its structure was determined from 2-D NMR experiments, and the stereochemistry of *r*-**11a** was confirmed by single-crystal X-ray diffraction (see Supporting Information). The GC-MS data of the product mixture revealed a minor compound (39 rel. %), which had the same molar mass as *r*-**11a** (M^+, m/z = 212) (see Figure S1). Its identity can be inferred by comparing fragmentation patterns in the mass spectra of the two GC peaks. The major product *r*-**11a** displays a strong base peak at m/z = 105, which is indicative of its benzoyl (Bz) group. The minor product wholly lacks this signature signal (see Figure S3). Thus, it cannot be configurational isomer *s*-**11a**. The minor compound decomposed during column chromatography. Either configurational isomer of constitutional isomer **12a** is a good candidate for its identity (Scheme 3a) because **12a** is an aldehyde that is expected to be unstable. Indeed, it is most likely stereoisomer *r*-**12a**, as will be explained.

1-{*rac*-(1*R*,2*R*,4*S*,5*S*,8*r*)-8-Phenyltricyclo[3.2.1.0^{2,4}]oct-8-yl}-ethan-1-one (*r*-**12b**; Scheme 3b) was formed after individual thermolyses of carbene **1** precursors *r*-**10** and *s*-**10** (Figure 4) in neat PhC(O)Me. The major product was isolated in 78% yield from *r*-**10** and 69% yield from *s*-**10**. Its structure was determined by 2-D NMR experiments, and the stereochemistry of *r*-**12b** was confirmed by single-crystal X-ray diffraction (see Supporting Information). The GC-MS data of the product mixture showed traces of a product (7 rel. %) with the same molar mass as *r*-**12b** (M^+, m/z = 226) (see Figure S2). Its identity can be inferred by comparing fragmentation patterns in the mass spectra of the two GC peaks. The minor product displays a strong base peak at m/z = 105 (see Figure S3), indicating the presence of a Bz group. Configurational isomer *s*-**12b** lacks this signal. Thus, either configurational isomer of constitutional isomers **11b** is a good candidate for its identity (Scheme 3b) because each has a Bz group.

Scheme 4 outlines a two-step mechanism to explain how carbene **1** and carbonyl compounds PhC(O)R [R = (a) H, (b) Me] react to produce compounds **11** and **12**. Initial Ad_N2 elementary steps generate the bent 1,3-zwitterion rotamers **14** and **17**, respectively. Neutral **14** and **17** undergo pinacolic rearrangement[116,117] in which the R (Scheme 4a) or Ph (Scheme 4b) group migrates to the vicinal C atom. Thus, a C−

Scheme 4. Addition of Nucleophilic Carbene 1 to Carbonyl Compounds PhC(O)R Followed By Neutral Pinacolic Rearrangement with Complete Diastereofacial Selectivity[a]



[a] R = (a) H, (b) Me.

Table 1. Structural Data for Reaction of 1 and PhC(O)H[a,b]

	tilt angle (°)[c]	$\Delta_{\text{rel}}G_{438.15}$ (kcal/mol)	$\bar{\nu}_{\text{TS}}$ (cm^{-1})	$\Delta G^{\ddagger}_{438.15}$ (kcal/mol)	partial charge[d]	μ (D)
1 + PhC(O)H	−30.5[e]	0			−0.052	[f]
13a	−36.0	20.3	120*i*	20.3	−0.009	5.45
14a	−37.3	16.1			0.175	7.58
15a	−22.6	16.8	326*i*	0.7	0.269	6.77
r-**11a**	1.8	−52.9			−0.301	2.65
16a	−35.0	21.3	124*i*	21.3	0.014	5.81
17a	−36.3	16.8			0.200	7.89
18a	−20.1	18.3	170*i*	1.6	0.316	6.63
r-**12a**	0.2	−43.6			−0.136	2.46

[a] See Figure 2a for atom numbering. [b] Data computed using the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) theoretical model. [c] Dihedral angle defined as $1/2[\omega(\text{C2}-\text{C1}-\text{C5}-\text{C8}) - \omega(\text{C6}-\text{C5}-\text{C1}-\text{C8})]$ of the tricyclo[3.2.1.0^{2,4}]oct-8-yl moiety. [d] Natural charge density of the C8 atom of the tricyclo[3.2.1.0^{2,4}]oct-8-yl moiety. [e] Tilt angle of singlet-state carbene ^{1}**1**. [f] $\mu(^1\mathbf{1})$ = 2.74 D and μ(PhC(O)H) = 3.32 D.

Table 2. Structural Data for the Reaction of 1 and PhC(O)Me[a,b]

	tilt angle (°)[c]	$\Delta_{\text{rel}}G_{438.15}$ (kcal/mol)	$\bar{\nu}_{\text{TS}}$ (cm^{-1})	$\Delta G^{\ddagger}_{438.15}$ (kcal/mol)	partial charge[d]	μ (D)
1 + PhC(O)Me	−30.5[e]	0			−0.052	[f]
13b	−36.2	23.8	139*i*	23.8	0.010	5.59
14b	−37.7	20.8			0.171	7.48
15b	−19.8	24.5	336*i*	3.7	0.311	6.35
r-**11b**	−0.5	−42.9			−0.106	2.56
16b	−35.1	24.7	142*i*	24.7	0.027	5.87
17b	−34.9	21.1			0.204	7.58
18b	−21.2	21.9	157*i*	0.8	0.314	6.45
r-**12b**	−0.1	−43.8			−0.133	2.38

[a] See Figure 2a for atom numbering. [b] Data computed using the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) theoretical model. [c] Dihedral angle defined as $1/2[\omega(\text{C2}-\text{C1}-\text{C5}-\text{C8}) - \omega(\text{C6}-\text{C5}-\text{C1}-\text{C8})]$ of the tricyclo[3.2.1.0^{2,4}]oct-8-yl moiety. [d] Natural charge density of the C8 atom of the tricyclo[3.2.1.0^{2,4}]oct-8-yl moiety. [e] Tilt angle of singlet-state carbene ^{1}**1**. [f] $\mu(^1\mathbf{1})$ = 2.74 D and μ(PhC(O)Me) = 3.05 D.

O double bond is reconstituted. The mechanism does not explain, however, the diastereoselective formation of *r*-**11** and *r*-**12** over *s*-**11** and *s*-**12**. Thus, computational chemistry was used to assess the feasibility of this two-step mechanism and to understand the stereochemistry. The equilibrium geometries of PhC(O)H, PhC(O)Me, ^{3}**1**, ^{1}**1**, **1**H$^+$, and **11**−**18** were computed using the B3LYP/6-31G(d) method. Vibrational analyses were done to ensure that each TS had one and only one imaginary frequency ($\bar{\nu}_{\text{TS}}$). Imaginary normal modes were animated to verify that they corresponded to the expected nuclear motions. Thermodynamic data were computed at the same level of theory as the geometry optimizations, and certain values were scaled according to established recommendations. The energies of stationary points were computed at the B3LYP/6-311G(d,p) level of theory. Further details are given in the Experimental Section and Supporting Information.

The data in Table 1 are consistent with the mechanism proposed in Scheme 4 (R = H). The C8 atom of carbene **1** donates electron density to PhC(O)H during the Ad$_{\text{N}}$2 step. Although the activation enthalpy ($\Delta H^{\ddagger}$) for the **1** + PhC(O)H → **14a** elementary step was computed to be negative[118−124] at −2.8 kcal/mol, the fairly high activation free energy ($\Delta G^{\ddagger}$) of 20.3 kcal/mol is due to the loss of degrees of freedom in TS **13a**, particularly at the elevated reaction temperature of 165 °C. Homoaromatic 1,3-zwitterion **14a** is bent toward the cyclopropane side to an even greater extent than is carbene **1** (vide

Table 3. Computed Geometries of *endo*-Tricyclo[3.2.1.$0^{2,4}$]oct-8-ylidene Triplet (^{3}1) and Singlet (^{1}1) and Its Conjugate Acid (1H$^+$) Reveal Substantial Bridge Bending[a,b]

	tilt angle (°)[c]	bridge angle (°)[d]	proton angle (°)[e]	r(C2−C3) (Å)[f]	r(C2−C8) (Å)[g]	r(C2−C4) (Å)	distance ratio[h]	μ (D)[i]
^{3}**1**	0.7	98.9		1.51	2.33	1.54	1.52	1.04
^{1}**1**	−30.5	98.8		1.49	1.96	1.69	1.16	2.74
1H$^+$	−41.4	107.0	4.8	1.50	1.81	1.93	0.94	2.30

[a] See Figure 2a for atom numbering. [b] Equilibrium geometries optimized using the (U)B3LYP/6-31G(d) method. [c] Dihedral angle defined as $1/2[\omega(\text{C2−C1−C5−C8}) - \omega(\text{C6−C5−C1−C8})]$. [d] Angle defined as θ(C1−C8−C5). [e] Dihedral angle defined as ω(C8−C1−C5−H8). [f] Distance equivalent to r(C4−C3). [g] Distance equivalent to r(C4−C8). [h] Trishomocyclopropyl index defined as r(C2−C8)/r(C2−C4). [i] Dipole moment computed using the (U)B3LYP/6-311G(d,p)//(U)B3LYP/6-31G(d) theoretical model.

infra). At that point in the two-step mechanism, the formerly divalent C atom of **1** has shed electron density and has become a carbonium ion center. The dipole moment (μ) of 1,3-zwitterion **14a** is 7.58 D. In the [1,2]-sigmatropic rearrangement step of the mechanism proposed in Scheme 4, the tilt angle and μ of TS **15a** decrease. The main bridge in product *r*-**11a** is tilted slightly away from the cyclopropane side. Its μ is within range of other carbonyl compounds. The divalent C atom of **1** is eventually bonded to the H atom of PhC(O)H to form a polar covalent C−H bond. Ultimately, the ΔG of the **1** + PhC(O)H system has been stabilized by 52.9 kcal/mol in the form of *r*-**11a**. A similar narrative can be made for the pinacolic[116,125] [1,2]-sigmatropic rearrangement leading to *r*-**12a** (Scheme 3a). However, the divalent C atom of **1** that is eventually incorporated into *r*-**12a** has bonded to the C_{ipso} atom of the Ph group of PhC(O)H, and the newly formed C−C covalent bond of *r*-**12a** is less polar than the corresponding C−H covalent bond of *r*-**11a** (Table 1). The computed migratory aptitudes of various groups during pinacolic rearrangements have been reported elsewhere.[125]

The equilibrium geometries of carbenes ^{1}**1** and ^{3}**1** were optimized using the (U)B3LYP/6-31G(d) method(s) (Table 3). The *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-8-ylium ion (1H$^+$) was modeled as well. It is the conjugate acid of carbene **1** and is needed to compute the proton affinity (PA) of **1**. Moreover, it represents the cationic portion of 1,3-zwitterions **14** and **17**. The optimal geometry and other properties of carbene **1** depend on its spin multiplicity, S_0 or T_1. Contour maps for their frontier MOs indicate that these electronic states are dominated by the closed-shell $^1(n^2p^0)$ and open-shell $^3(n^1p^1)$ electron configurations, respectively. Table 3 shows that the bicoordinate C atom bridge angles of ^{1}**1** and ^{3}**1** are essentially the same. Given that triplet carbenes typically adopt wider bond angles than do their singlet counterparts, it is not surprising that ^{3}**1** has more internal energy than that of ^{1}**1**. Because the bridge angle θ(C1−C8−C5) of ^{1}**1** is 98.8° (Table 3), the n-orbital is $sp^{0.36}$ hybridized (eq 1) with 73% s-character (eq 2). Thus, filling the low-energy orbital with both nonbonding electrons is stabilizing even though electron−electron repulsion is mitigated in ^{3}**1**. Trishomocyclopropyl stabilization within ^{1}**1** would be lost if an n-orbital electron (Figure 3b) were to be promoted to the p-orbital (Figure 3c), which is part of a triangular array of basis set p-orbitals. The net effect to the three-center two-electron bond is antibonding (Figure 3a). Hence, ^{3}**1** is destabilized over ^{1}**1**. An experimentally corrected singlet−triplet energy gap for carbene **1** ($\Delta E_{S-T}(\mathbf{1})_{corr}$) was computed using the (U)B3LYP/6-311G(d,p)//(U)B3LYP/6-31G(d) theoretical model and eqs S1−S3. The computed $\Delta E_{S-T}(CH_2)$ (eq S1) is 12.1 kcal/mol.[126] This is 2.9 kcal/mol above the experimental value of 9.215 kcal/mol.[126] Assuming that the E values for carbene **1** would also be too positive, subtracting this discrepancy from the initially computed value of −22.4 kcal/mol (eq S2) gives $\Delta E_{S-T}(\mathbf{1})_{corr} = -25.2$ kcal/mol (eq S3), which is in accordance with previous reports.[27,28] The large computed ΔE_{S-T} clearly shows a pronounced reversal of the usual ordering of the lowest T and S states of dialkylcarbenes because the value is large and negative as defined herein. For comparison, the corrected ΔE_{S-T} of carbene **2** is −27.1 kcal/mol, according to the (U)B3LYP/6-311+G(3df,2p)//(U)B3LYP/6-31G(d) theoretical model.[27] The magnitude of ΔE_{S-T} is far from the ∼65 kcal/mol boundary between carbenes (i.e., 1,1-zwitterions) and ylides (1,2-zwitterions).[127] However, ^{1}**1** is nucleophilic and expected to participate in polar mechanisms.

$$\text{hybridization of n-orbital} = sp^{-2\left(\frac{\cos\theta}{1+\cos\theta}\right)} \tag{1}$$

$$\text{s-character} = \left(\frac{1+\cos\theta}{1-\cos\theta}\right) \times 100\% \tag{2}$$

The parameters listed in Table 3 clearly demonstrate that Lewis structures cannot adequately depict bonding in ^{1}**1** and 1H$^+$. For example, the C2−C4 bond of ^{3}**1** is of normal length for C−C single bonds (i.e., r = 1.54 Å), but that of ^{1}**1** is unusually long at r = 1.69 Å (see Table 3). Moreover, the bridge of ^{3}**1** is essentially untilted, whereas that of carbene ^{1}**1** is significantly bent toward the cyclopropane despite an increase in strain. The associated bridge in carbocation 1H$^+$ is predicted to be tilted toward the C2−C4 σ/π-bond by −41.4° (Table 3). Because electron density is being drawn away from the σ/π-

$$\underline{\mathbf{B}}\text{−}H^{+} \xrightarrow{\Delta H^{\circ}_{PA}} H^{+} + \underline{\mathbf{B}}\!: \tag{3}$$

Table 4. Reactivity Data[a,b]

compound	PA (kcal/mol)	E_{HOMO} (eV)	E_{LUMO} (eV)	$-\chi$ (eV)	η (eV)	ΔN	$\Delta E_{(n\rightarrow\pi^*)}$ (eV)	$\Delta E_{(p\leftarrow n)}$ (eV)	$\Delta\Delta E$ (eV)
1	272	−5.22	0.43	−2.39	2.83				
PhC(O)H	204	−7.17	−1.99	−4.58	2.59	−0.20	3.22	7.61	−4.38
PhC(O)Me	210	−6.98	−1.77	−4.37	2.61	−0.19	3.45	7.42	−3.97

[a] Computed using the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) theoretical model. [b] MO energy gap defined as $\Delta E_{\text{carbene}\rightleftharpoons\text{PhC(O)R}}$ [R = (a) H, (b) Me].

bonds of **1** and **1**H$^+$ toward the electron-deficient C8 atoms, the effect is understandably more pronounced in the cation. The distance ratio for **1**H$^+$ is close to unity (i.e., 0.94; Table 3). Trishomocyclopropyl stabilization is optimal in an equilateral triangle (see Figure S16). Finally, $\mu(^3\mathbf{1})$ is unremarkable, whereas that of $^1\mathbf{1}$ is quite large for a hydrocarbon (μ = 2.74 D; Table 3). The carbonyl compounds are only slightly more polar at μ(PhC(O)H) = 3.32 D and μ(PhC(O)Me) = 3.05 D.

The Brønsted−Lowry basicity of foiled carbene **1** is informative because nucleophilicity often parallels basicity. The protolysis reaction of carbenium ion **1**H$^+$ (eq 3; **B** = **1**) is the reverse of the PA reaction of the carbene conjugate base. The gas-phase PA value for carbene **1** was computed using the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) theoretical model. Although foiled carbene **1** has only a cyclopropane "functional group,"[128] its PA value of 272 kcal/mol places it among the most Brønsted−Lowry basic carbenes.[129] It is clear from the PA values in Table 4 that foiled carbene **1** is a better electron-pair donor than are the PhC(O)R compounds because their PA values are lower.

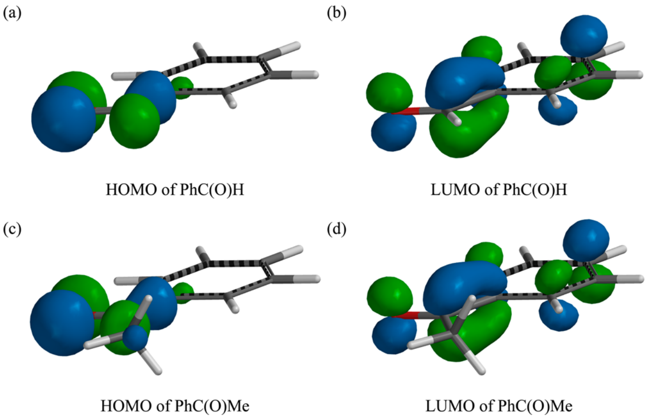
The Lewis basicity of the n-orbitals of **1** and PhC(O)R can be evaluated using the hard and soft acid and base (HSAB)[130,131] principle. After calculating the hardness (η) (eq 4) and absolute electronegativity (χ) (eq 5) of the acid and base from their frontier orbital energies, the direction and (fractional) number of electrons transferred (ΔN) in the initial Acid (A)/Base (B) interaction (eq 6) (e.g., carbene **1**/PhC(O)R) can be assessed semiquantitatively.[130] Note that **1** is considered to be the acid in eq 6. This assumption is reasonable because **1** is electron-deficient and should therefore act as the electron-pair acceptor. However, the *negative* ΔN values listed in Table 4 indicate that the roles are *reversed*. The carbonyl compounds are the acids, and carbene **1** is the base. Additionally, the magnitude of ΔN is fairly large compared with other nucleophilic carbenes.[97] This indicates significant electron flow from the carbene to the carbonyl compounds.

$$\text{hardness}(\eta) = 1/2(E_{\text{LUMO}} - E_{\text{HOMO}}) \tag{4}$$

$$\text{absolute electronegativity}\,(\chi) = 1/2(E_{\text{LUMO}} + E_{\text{HOMO}}) \tag{5}$$

$$\text{electrons transferred}\,(\Delta N) = 1/2\left(\frac{\chi_{\text{A}} - \chi_{\text{B}}}{\eta_{\text{A}} + \eta_{\text{B}}}\right) \tag{6}$$

The difference in energy differentials ($\Delta\Delta E$) between the frontier MOs of carbenes and their reaction partners indicates which HOMO−LUMO interaction is dominant.[77,78] Thus, the philicity of carbene **1** toward carbonyl compounds can be categorized by the vector quantity defined in eq 7. The calculated negative values $\Delta\Delta E$(PhC(O)H) = −4.38 eV and $\Delta\Delta E$(PhC(O)Me) = −3.97 eV (Table 4) further attest to the nucleophilicity of carbene **1**. Recall that carbonyl ylides are formed when the empty p-orbital of an electrophilic carbene interacts with the high-lying n-orbital of the carbonyl group's O atom (i.e., p ← n). The frontier MOs of PhC(O)H and PhC(O)Me are presented in Figure 5 and can be compared to those of carbene **1** (Figure 3b and c). This step is reversible because independently formed carbonyl ylides can fragment to afford electrophilic carbenes.[132−134] However, given the PA, HSAB, and frontier MO interaction $\Delta\Delta E$ results (Table 4), and the body of evidence that carbonyl ylide formation involves electrophilic carbenes,[95] a mechanism involving carbonyl ylide reaction intermediates can be ruled out.



HOMO of PhC(O)H
LUMO of PhC(O)H
HOMO of PhC(O)Me
LUMO of PhC(O)Me

Figure 5. Frontier MOs of benzaldehyde (PhC(O)H) and acetophenone (PhC(O)Me) (surfaces shown with a 0.07 isovalue computed using the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) theoretical model.).

$$\Delta\Delta E = \Delta E_{(\text{n}\to\pi^*)_{\text{nucleophilic}}} - \Delta E_{(\text{p}\leftarrow\text{n})_{\text{electrophilic}}} \tag{7}$$

1,3-Zwitterions are generally thought to be generated when the bicoordinate C atom of a nucleophilic carbene bonds with the C atom of an electrophilic carbonyl group.[135−137] Thus, the $\text{Ad}_\text{N}2$ of carbene **1** and PhC(O)H should yield **14a** and **17a** (Scheme 4). A conformational analysis was performed using a rigid grid calculation at the B3LYP/6-31G(d) level of theory (Figure 6). The dihedral angles for tilting (see Table 1) and for >C8$^+$−CH(O$^-$)Ph bond rotation were varied while maintaining the bond at r = 1.55 Å. Pools of stability were found for the **14a** and **17a** rotamers (Figure 6). Indeed, trishomocyclopropyl stabilization is predicted to be influential in the *anti*-O conformation with a tilt angle of approximately −33°. Thus, rotation around the pivotal >C8$^+$−CH(O$^-$)Ph bond is facile. Note that the tricyclo[3.2.1.0^{2,4}]oct-8-ylium subunits of **14a** and **17a** are nonclassical carbocations.[138−152,160] Their tilt angles of −37.3° and −36.3° (Table 1), respectively, are greater than that of **1** and almost as much as **1**H$^+$ (Table 3).

The carbonyl compounds might experience steric hindrance during the addition reactions to the divalent C atom of **1**. If singlet-state carbene $^1\mathbf{1}$ were untilted then the π-plane divided accessible space (PDAS)[153] values of its *anti* and *syn* faces, with respect to the cyclopropane, would be nearly equal. Obstruction from the exocyclic H6 and H7 atoms would be similar to that from the H2 and H4 atoms. Thus, the ratios *r*-**11**:*s*-**11** and *r*-**12**:*s*-**12** would each be close to unity. Because this is not the case and only *r*-**11** and *r*-**12** were formed (Scheme 3), the complete stereoselectivity that was observed in the reaction of **1** and PhC(O)R must be due to another reason. The PDAS of carbene **1** will clearly be greater on its *anti* face than on its *syn* face because the molecule is significantly tilted toward the cyclopropane side (Figure 3). This phenomenon is predicted to exist in the bent homoaromatic 1,3-zwitterions **14** and **17** (Scheme 4) to an even greater extent according to the DFT model (Tables 1 and 2). The *syn* lobes of the p-orbitals of the C8 atoms of **14** and **17** are engaged with the σ/π-bonds of the nearby cyclopropane edges in a three-center two-electron bond. The inner lobes are shielded from nucleophilic impingement as well. Thus, only the outer lobes of the p-orbitals of the C8 atoms in **14** and **17** can receive electron density from the

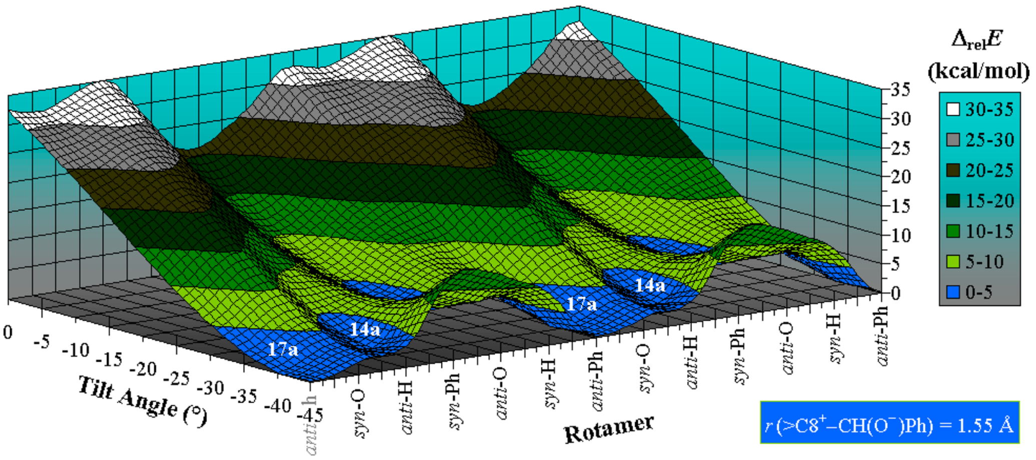


Figure 6. A conformational analysis of 1,3-zwitterions **14a**/**17a** was performed using rigid grid calculations at the B3LYP/6-31G(d) level of theory. Rotation of 720° around the $>C8^+-CH(O^-)Ph$ bond is shown for illustrative purposes. The surface exhibits pools of stability (blue) at large tilt angles.

electron-donating groups migrating in the [1,2]-sigmatropic rearrangements (Scheme 4). Because the tricyclo[3.2.1.$0^{2,4}$]oct-8-yl frameworks of the 1,3-zwitterions are locked into place due to the homoaromatic stabilization, group migrations during the pinacolic rearrangements can proceed only along the *anti* faces of **14** and **17**, giving *r*-**11** and *r*-**12**, respectively. Formation of *s*-**11** and *s*-**12** is difficult but not precluded. Hence, the pinacolic rearrangements are highly stereoselective but not stereospecific. Strict stereoelectronic control of the [1,2]-sigmatropic rearrangements leads to complete diastereofacial selectivity.[71,154−162] Note that these pinacolic rearrangements proceed under neutral conditions because **14** and **17** are not cations. They are inner salts.

The two-step mechanism accounts for the product mixtures that were revealed by GC-MS. Considerable product formation from a competitive 1,2-Ph migration is expected to occur for the reaction of carbene **1** with PhC(O)H because the Ph group has a relatively high migratory aptitude.[162−164] This would form aldehyde *r*-**12a** (Scheme 3a). It is akin to ketone *r*-**12b** (Scheme 3b), which also stems from Ph migration. Indeed, the fragmentation pattern in the mass spectrum of provisionally identified *r*-**12a** corresponds to that of ketone *r*-**12b** (see Figure S3). Similarly, the minor product formed by the reaction of carbene **1** with PhC(O)Me should be *r*-**11b** (Scheme 3b). It stems from 1,2-Me migration, which is akin to the 1,2-H migration that yields *r*-**11a** (Scheme 3a). The general fragmentation patterns observed in the mass spectra for *r*-**11a** and *r*-**11b** match well. Each has the Bz group as its base peak. The low yield of compound *r*-**11b** compared with that of *r*-**12b** confirms that the aptitude for the Me group migration is substantially lower than that for Ph groups.[163] The results herein indicate a relative migratory aptitude of H > Ph ≫ Me. Unlike the H atom, the Me group resists migration because its C atom is less apt to adopt positive charge. The unsaturated Ph group, on the other hand, is more capable because its π-electrons delocalize the positive charge.

■ CONCLUSIONS

The condensed-phase reactivity of the foiled carbene *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-8-ylidene (**1**) with carbonyl compounds PhC(O)R [R = (a) H, (b) Me] was the main focus of this investigation. Carbene reaction intermediate **1** was generated by thermally decomposing each diastereomer of oxadiazoline **10**. Only solvolysis reactions were observed in each liquid (i.e., aldehyde PhC(O)H or ketone PhC(O)Me). The hypothesized primary adducts underwent pinacolic rearrangements that reestablish the carbonyl functional groups. The identities of the major products *r*-**11a** from PhC(O)H and *r*-**12b** from PhC(O)Me were confirmed by 2-D NMR spectroscopy and single-crystal X-ray diffraction. Mainly, a H atom or Ph group had migrated to the originally divalent C atom of **1**. In the case of PhC(O)H, competitive Ph group migration was argued to give a lesser amount of an unisolated constitutional isomer *r*-**12a**. It lacks the Bz group that is expected in the configurational isomer *s*-**11a**. With PhC(O)Me, scant Me group migration gave traces of an unisolated constitutional isomer *r*-**11b** possessing the Bz group. The absence of products formed via *syn*-periplanar migration (e.g., *s*-**11a**) indicates that the pinacolic rearrangements are under strict stereoelectronic control.

Synergy between the divalent C atom and embedded *endo*-fused cyclopropane of **1** greatly influences its structural, electronic, and reactive nature. The p-orbital of the divalent C atom of carbene **1** participates in a three-center two-electron bond making **1** trishomoaromatic. The effect is pronounced because the C1−C8−C5 main bridge of carbene **1** is tilted 31° toward the electron-releasing C2−C4 σ/π-bond, which was computed to be 1.69 Å long. The equilibrium geometry of carbene **1** as well as the contours and energies of its key MOs were computed and presented in order to support this hypothesis. The most noteworthy effect is upon the philicity of carbene **1**. Attenuation of its electron-deficiency is due to the carbene's trishomocyclopropyl HOMO{−1}, which involves the p-orbital that is also prominent in the LUMO. The slightly negative partial charge of the divalent C atom of **1** is consistent with a carbene that is computed to be remarkably Brønsted−Lowry basic. The computed gas-phase PA of **1** is 272 kcal/mol. It is high compared with other carbenes and certainly to the carbonyl compounds (Table 4). The nucleophilicity of **1** is also predicted by comparing its frontier MO energies with those of the carbonyl compounds used in this study (see Table 4). The results indicate a predilection for **1** to react using its HOMO, which is its localized n-orbital. The carbonyl compounds accept the electron pair into their LUMOs, which comprise the C−O π^*-antibonds. This points to a mechanism in which **1** initially impinges upon the C atom of carbonyl compounds PhC(O)R [R = (a) H, (b) Me] in an Ad_N2 elementary step to form highly bent homoaromatic 1,3-zwitterions **14** and **17**. These unstable reaction intermediates undergo pinacolic [1,2]-sigmatropic rearrangements in the neutral reaction conditions. The remarkable stereocontrol behind the formation of just one stereoisomer of constitutional isomers **11** and **12** (i.e., *r*-**11** and *r*-**12**) was traced back to the special topologies of **14** and **17**. The results affirm that homoconjugation between a properly situated noncontiguous cyclopropane and a divalent C atom produces a nucleophilic foiled carbene.

■ EXPERIMENTAL SECTION

Computational Methods. Quantum chemical calculations were performed using the *Spartan'14 Parallel Suite* computer program.[165] Single-determinant HF wave functions were corrected for electron−electron correlation using DFT. Each molecule's equilibrium geometry and single-point energy (E) was computed using the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) theoretical model:[166,167] exchange = 0.20 HF + 0.08 Slater + 0.72 Becke and correlation = 0.81 LYP + 0.19 VWN1-RPA.[168] The E values at $T = 0$ K and $p = 0$ atm were converted to enthalpy (H) values at $T = 298.15$ or 438.15 K and $p = 1.00$ atm using eq S4 (see Supporting Information) and vibrational frequencies derived from a harmonic approximation of geometry-optimized structures. The temperature-independent zero-point vibrational energy (ZPVE)[169] and thermal vibrational energy ($\Delta_{\text{vib}}H$) values for each gas-phase molecule were scaled by recommended factors z and h (eq S4), respectively ($T = 298$ K: z = 0.9826 and h = 1.0004; $T = 450$ K: z = 0.9826 and h = 0.9895).[170] The increase in kinetic energy, due to translations (3(1/2)RT) and rotations (3(1/2)RT) for each nonlinear molecule was also added to E. Finally, RT (i.e., "pV work" needed to expand one mole of ideal gas to $V = 24.4654$ L at $T = 298.15$ K or $V = 35.954$ L at $T = 438.15$ K) was added to E to obtain H (eq S4). The H values of **1** and PhC(O)R [R = (a) H, (b) Me] were added, and the sum was subtracted from the H value of each molecule of interest to obtain ΔH. The thermal vibrational component (S_{vib}) value of total entropy (S) was scaled by recommended factor s (eq S5) ($T = 298$ K: s = 1.0029; $T = 450$ K: s = 0.9969).[170] The S values of **1** and PhC(O)R [R = (a) H, (b) Me] were added, and the sum was subtracted from the S value of each molecule of interest to obtain ΔS. Gibbs free energy (ΔG) values of molecules were computed relative to the combined G value of the **1** + PhC(O)R reference state at specified temperatures according to eq S5. Note that the $\Delta H^{\ddagger}$ values for the intermolecular addition reactions of carbene **1** with the carbonyl compounds were negative. This is not unusual for carbenes.[118−124] Although carbene reactions are enthalpically favorable, a specifically oriented TS is sometimes required. This decreases the activation entropy ($\Delta S^{\ddagger}$) and is not thermodynamically favorable. Additionally, bringing two molecules together to afford one less molecule in the *TS* also represents a loss in $\Delta S^{\ddagger}$. Thus, when $\Delta S^{\ddagger}$ and the high reaction temperature are taken into account, the overall $\Delta G^{\ddagger}$ values were always positive.

General Information. Melting points were measured on a melting point microscope and are uncorrected. The FT-NMR spectra were recorded at $T = 300$ K while applying the following radio frequencies: $\nu(^1H) = 400.1$ MHz and $\nu(^{13}C) = 100.6$ MHz or $\nu(^1H) = 600.1$ MHz and $\nu(^{13}C) = 150.9$ MHz. Proton and carbon-13 chemical shift (δ) values are reported relative to tetramethylsilane (TMS), although the deuterated solvents used were not doped with that internal standard. Instead, the solvent's residual peak was used to calibrate the ^{1}H and ^{13}C NMR spectra: $\delta_H(CDCl_3) = 7.26$ ppm and $\delta_C(CDCl_3) = 77.16$ ppm. Structural assignments were made based on the following gradient-enhanced 2-D NMR experiments: HMQC, HMBC, COSY, and NOESY. The FT-IR spectra were measured using the ATR sampling technique. Results are reported in wavenumbers (cm^{-1}). Accurate masses were obtained using ESI techniques on an HRMS mass spectrometer outfitted with a TOF analyzer. Single-crystal XRD analyses were done using a diffractometer equipped with a CCD detector and a low temperature device ($T = 90−300$ K). Tandem GC-MS analyses were conducted by carrying a split sample with He gas through a 30-m poly(methylphenylsiloxane) capillary column (95% dimethyl/5% diphenyl, 0.25 mm i.d., and 0.25-μm film-thickness) ending with an EI mass-selective detector (70 eV). Results are reported as m/z (% relative intensity). Elemental analyses were performed using standard techniques.

General Settings for GC-MS Analysis. Pressure: 0.416 bar. Flow: 0.7 mL/min. Average velocity: 32 cm/s. Injection volume: 1.0 μL. Split ratio: 25:1. Injection temperature: 270 °C. Starting temperature: 80 °C for 2 min. Ramp: 5 °C/min up to 145 °C. Ramp: 15 °C/min up to 220 °C. Isotherm: 220 °C for 3 min. Ramp: 15 °C/min up to 270 °C. Isotherm: 270 °C for 3 min.

Materials. Oxadiazolines *r*-**10** and *s*-**10** were prepared and identified according to published methods.[25] Freshly distilled benzaldehyde (PhC(O)H) and acetophenone (PhC(O)Me) were dried over active 4-Å molecular sieves prior to use. Other commercially available compounds were used without further purification. Analytical thin-layer chromatography (TLC) was performed on aluminum plates with silica gel 60 F_{254}. Spots were visualized using either an I_2 chamber or a UV lamp ($\lambda = 254$ nm). Flash chromatography was performed with a silica gel 60 (230−400 mesh) stationary phase and a hexane/EtOAc mobile phase.

Phenyl{*rac*-(1*R*,2*R*,4*S*,5*S*,8*r*)-tricyclo[3.2.1.0^{2,4}]oct-8-yl}methanone (*r*-11a). From thermolysis of *r*-**10**: ***CAUTION!*** A solution of oxadiazoline *r*-**10** (0.098 g, 0.471 mmol) in PhC(O)H (4.5 mL) was stirred in a pressure tube for 6 h at $T = 165$ °C, and the product was isolated by column chromatography using hexane/EtOAc (4:1) eluant to yield *r*-**11a** (0.053 g, 53%) as a white solid. From thermolysis of *s*-**10**: ***CAUTION!*** A solution of oxadiazoline *s*-**10** (0.150 g, 0.720 mmol) in PhC(O)H (5 mL) was stirred in a pressure tube for 4 h at $T = 165$ °C, and the product was isolated by column chromatography using hexane/EtOAc (4:1) eluant to yield *r*-**11a** (0.065 g, 43%) as a white solid. Mp 45−50 °C; δ_H (400.1 MHz, $CDCl_3$) 0.79−0.86 (1 H, m), 1.11−1.15 (1 H, m), 1.23−1.30 (2 H, m), 1.50−1.52 (2 H, m), 1.61−1.69 (2 H, m), 2.66−2.72 (2 H, m), 3.54−3.58 (1 H, m), 7.43−7.48 (2 H, m), 7.51−7.57 (1 H, m), 7.96 (2 H, m); δ_C (100.6 MHz, $CDCl_3$) 17.4 (CH_2), 22.4 (2× CH), 27.1 (2× CH_2), 40.7 (2× CH), 74.5 (CH), 128.3 (2× CH), 128.5 (2× CH), 132.6 (CH), 137.8 (C), 200.3 (C); $\bar{\nu}$ (solid) 3057 (w), 2964 (m), 2876 (w), 1718 (m), 1673 (s), 1596 (w), 1477 (w), 1446 (m), 1353 (m), 1312 (m), 1297 (m), 1271 (m), 1219 (s), 1122 (m), 1020 (m), 868 (m), 846 (m), 821 (m), 907 (s), 744 (m), 691 (s), 670 (m); m/z (EI, 70 eV) 212 (M$^+$, 12), 197 (2), 183 (10), 115 (6), 170 (19), 157 (32), 144 (42), 129 (7), 121 (12), 115 (13), 105 (100), 92 (50), 77 (69), 65 (5), 51 (13); HRMS (ESI-TOF) found [M + Na]$^+$ 235.1093, $C_{15}H_{16}ONa$ requires 235.1099; Anal. Calcd for $C_{15}H_{16}O$ C 84.87, H 7.60; found C 84.46, H 7.58.

1-{*rac*-(1*R*,2*R*,4*S*,5*S*,8*r*)-8-Phenyltricyclo[3.2.1.0^{2,4}]oct-8-yl}-ethan-1-one (*r*-12b). From thermolysis of *r*-**10**: ***CAUTION!*** A solution of oxadiazoline *r*-**10** (0.104 g, 0.499 mmol) in PhC(O)Me (5 mL) was stirred in a pressure tube for 4 h at $T = 165$ °C, and the product was isolated by column chromatography using hexane/EtOAc (4:1) eluant to yield ketone *r*-**12b** (0.088 g, 78%) as a white solid. From thermolysis of *s*-**10**: ***CAUTION!*** A solution of oxadiazoline *s*-**10** (0.150 g, 0.720 mmol) in PhC(O)Me (7 mL) was stirred in a pressure tube for 4 h at $T = 165$ °C, and the product was isolated by column chromatography using hexane/EtOAc (4:1) eluant to yield ketone *r*-**12b** (0.113 g, 69%) as a white solid. Mp 133−136 °C; δ_H (600.1 MHz, $CDCl_3$) 0.79−0.84 (1 H, m), 1.08−1.13 (2 H, m), 1.18−1.22 (1 H, m), 1.39−1.44 (2 H, m), 1.56−1.60 (2 H, m), 2.17 (3 H, s), 3.02−3.05 (2 H, m), 7.19−7.23 (1 H, m), 7.27−7.31 (2 H, m), 7.33−7.36 (2 H, m); δ_C (150.9 MHz, $CDCl_3$) 16.8 (CH_2), 21.8 (2× CH), 24.8 (2× CH_2), 27.0 (CH_3), 41.7 (2× CH), 90.8 (C), 127.0 (CH), 128.7 (2× CH), 128.7 (2× CH), 138.9 (C), 209.6 (C); $\bar{\nu}$ (solid) 3046 (w), 2931 (w), 1688 (s), 1597 (w), 1477 (w), 1454 (w), 1356 (m), 1312 (m), 1229 (m), 1124 (m), 1038 (m), 937 (w), 899 (w), 792 (m), 750 (m), 695 (s) cm^{-1}; m/z (EI, 70 eV) 226 (M$^+$, 3), 211 (5), 197 (7), 183 (15), 172 (25), 158 (41), 144 (100), 129 (37), 115 (33), 105 (9), 91 (36), 79 (24), 65 (6), 51 (6); HRMS (ESI-TOF) found [M + Na]$^+$ 249.1254, $C_{16}H_{18}ONa$ requires 249.1255; Anal. Calcd for $C_{16}H_{18}O$ C 84.91, H 8.02; found C 84.71, H 7.77.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01988.

> NMR spectra for all new compounds and computational data for PhC(O)H, PhC(O)Me, ^{1}**1**, ^{3}**1**, **1**H^{+}, and **11**–**18** (PDF)
>
> CIF files X-ray crystallographic data of *r*-**11a** and *r*-**12b** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: udo.brinker@univie.ac.at; ubrinker@binghamton.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Dedicated to Professor Dr. Wolfgang Kirmse of the Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum, Bochum, Germany. Helpful discussions with Professor Barry K. Carpenter of the School of Chemistry, Cardiff University, Cardiff, United Kingdom, regarding the computational aspects of this report are much appreciated. We thank Alexander Roller of the Institute of Inorganic Chemistry, University of Vienna, for verifying the structures of compounds *r*-**11a** and *r*-**12b** by single-crystal X-ray diffraction.

■ REFERENCES

(1) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, 1977; Vol. *1*, Chapter 3, pp 109–198.

(2) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 2046–2048.

(3) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781–932.

(4) Rauk, A. *Orbital Interaction Theory of Organic Chemistry*, 2nd ed.; Wiley-Interscience: New York, 2001; pp 114–120, 165, 166, 206–208.

(5) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475–1485.

(6) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964.

(7) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971.

(8) *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. *1*.

(9) *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. *2*.

(10) *Methoden der Organischen Chemie (Houben-Weyl)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. *E19b*.

(11) *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI: Greenwich, CT, 1994; Vol. *1*.

(12) *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI: Stamford, CT, 1998; Vol. *2*.

(13) *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Elsevier: Amsterdam, 2001; Vol. *3*.

(14) *Contemporary Carbene Chemistry*; Moss, R. A., Doyle, M. P., Eds.; Wiley: Hoboken, NJ, 2014.

(15) Rouhi, A. M. *Chem. Eng. News* **1999**, *77* (36), 28–32.

(16) Wöhler, F. *Ann. Phys.* **1828**, *12*, 253–256.

(17) *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*; Bertrand, G., Ed.; Dekker: New York, 2002.

(18) Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457–5460.

(19) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485–1499.

(20) Chen, B.; Rogachev, A.; Yu; Hrovat, D. A.; Hoffmann, R.; Borden, W. T. *J. Am. Chem. Soc.* **2013**, *135*, 13954–13964.

(21) Bachrach, S. M. *Computational Organic Chemistry*, 2nd ed.; Wiley: Hoboken, NJ, 2014; p 297.

(22) Su, K.-J.; Pačar, M.; Mieusset, J.-L.; Arion, V. B.; Brinker, U. H. *J. Org. Chem.* **2011**, *76*, 7491–7496.

(23) Mieusset, J.-L.; Brinker, U. H. *J. Am. Chem. Soc.* **2006**, *128*, 15843–15850.

(24) Roth, H. D.; Sauers, R. R. *J. Phys. Org. Chem.* **2015**, *28*, 88–96.

(25) Apeland, I. M.; Kählig, H.; Lorbeer, E.; Brinker, U. H. *J. Org. Chem.* **2013**, *78*, 4879–4885.

(26) Freeman, P. K.; Dacres, J. E. *J. Org. Chem.* **2003**, *68*, 1386–1393.

(27) Freeman, P. K.; Pugh, J. K. *J. Org. Chem.* **2000**, *65*, 6107–6111.

(28) Freeman, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 1619–1620.

(29) Brinker, U. H.; Ritzer, J. *J. Am. Chem. Soc.* **1981**, *103*, 2116–2119.

(30) Moss, R. A.; Dolling, U.-H.; Whittle, J. R. *Tetrahedron Lett.* **1971**, *21*, 931–934.

(31) Mieusset, J.-L.; Brinker, U. H. *J. Org. Chem.* **2006**, *71*, 6975–6982.

(32) Winstein, S. In *Carbonium Ions: Major Types (Continued)*; Olah, G. A., Schleyer, P. v. R., Eds.; Reactive Intermediates in Organic Chemistry; Wiley-Interscience: New York, 1972; Vol. 3, Chapter 22, pp 965–1005.

(33) Story, P. R.; Clark, B. C., Jr. In *Carbonium Ions: Major Types (Continued)*; Olah, G. A., Schleyer, P. v. R., Eds.; Reactive Intermediates in Organic Chemistry; Wiley-Interscience: New York, 1972; Vol. 3, Chapter 23, pp 1007–1098.

(34) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809–886.

(35) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978; p 373.

(36) Story, P. R. *J. Am. Chem. Soc.* **1961**, *83*, 3347–3349.

(37) Conlin, R. T.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 7637–7638.

(38) Martella, D. J.; Jones, M., Jr.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 2896–2897.

(39) Jones, M., Jr. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI: Stamford, CT, 1998; Vol. *2*, pp 77–96.

(40) Murahashi, S.-I.; Okumura, K.; Kubota, T.; Moritani, I. *Tetrahedron Lett.* **1973**, *14*, 4197–4200.

(41) Murahashi, S.-I.; Okumura, K.; Maeda, Y.; Sonoda, A.; Moritani, I. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2420–2425.

(42) Okumura, K.; Murahashi, S.-I. *Tetrahedron Lett.* **1977**, *18*, 3281–3284.

(43) Freeman, P. K.; Raghavan, R. S.; Kuper, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 5288–5290.

(44) Freeman, P. K.; Hardy, T. A.; Raghavan, R. S.; Kuper, D. G. *J. Org. Chem.* **1977**, *42*, 3882–3892.

(45) Baird, M. S.; Reese, C. B. *J. Chem. Soc., Chem. Commun.* **1972**, 523–524.

(46) Skattebøl, L. *Tetrahedron* **1967**, *23*, 1107–1117.

(47) Holm, K. H.; Skattebøl, L. *J. Am. Chem. Soc.* **1977**, *99*, 5480–5481.

(48) Mieusset, J.-L.; Abraham, M.; Brinker, U. H. *J. Am. Chem. Soc.* **2008**, *130*, 14634–14639.

(49) Moss, R. A.; Ho, C.-T. *Tetrahedron Lett.* **1976**, *17*, 1651–1654.

(50) Moss, R. A.; Dolling, U.-H. *Tetrahedron Lett.* **1972**, *13*, 5117–5120.

(51) Kirmse, W.; Meinert, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1065–1066.

(52) Kirmse, W. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI: Stamford, CT, 1998; *Vol. 2*, Chapter 1, pp 1–50.

(53) Mieusset, J.-L.; Brinker, U. H. *J. Org. Chem.* **2008**, *73*, 1553–1558.

(54) Jones, W. M.; LaBar, R. A.; Brinker, U. H.; Gebert, P. H. *J. Am. Chem. Soc.* **1977**, *99*, 6379–6391 ; see footnote 27.

(55) Haerizade, B. N.; Kassaee, M. Z.; Zandi, H.; Koohi, M.; Ahmadi, A. A. *J. Phys. Org. Chem.* **2014**, *27*, 902–908.

(56) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162–2187.

(57) Wanzlick, H.-W.; Kleiner, H.-J. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 65.
(58) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725−728.
(59) Buron, C.; Gornitzka, H.; Romanenko, V.; Bertrand, G. *Science* **2000**, *288*, 834−836.
(60) Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621−622.
(61) Couture, P.; Pole, D. L.; Warkentin, J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1565−1570.
(62) Wanzlick, H. W. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 75−80.
(63) Lemal, D. M.; Lovald, R. A.; Kawano, K. I. *J. Am. Chem. Soc.* **1964**, *86*, 2518−2519.
(64) Breslow, R. *J. Am. Chem. Soc.* **1957**, *79*, 1762−1763.
(65) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719−3726.
(66) Stetter, H.; Kuhlmann, H. *Org. Synth.* **1984**, *62*, 170−178.
(67) Wöhler, F.; von Liebig, J. *Ann. Pharm. (Lemgo, Ger.)* **1832**, *3*, 249−282.
(68) Lapworth, A. *J. Chem. Soc., Trans.* **1903**, *83*, 995−1005.
(69) Lapworth, A. *J. Chem. Soc., Trans.* **1904**, *85*, 1206−1214.
(70) He, Y.; Xue, Y. *J. Phys. Chem. A* **2010**, *114*, 9222−9230.
(71) Pole, D. L.; Warkentin, J. *J. Org. Chem.* **1997**, *62*, 4065−4067.
(72) Venneri, P. C.; Warkentin, J. *J. Am. Chem. Soc.* **1998**, *120*, 11182−11183.
(73) Dawid, M.; Warkentin, J. *Can. J. Chem.* **2003**, *81*, 598−606.
(74) Wanzlick, H.-W.; Ahrens, H. *Chem. Ber.* **1964**, *97*, 2447−2450.
(75) Arduengo, A. J., III; Calabrese, J. C.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Tamm, M.; Schmutzler, R. *Helv. Chim. Acta* **1999**, *82*, 2348−2364.
(76) Mieusset, J.-L.; Schrems, A.; Abraham, M.; Arion, V. B.; Brinker, U. H. *Tetrahedron* **2009**, *65*, 765−770.
(77) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58−64.
(78) Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15−21.
(79) Moss, R. A. In *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*; Bertrand, G., Ed.; Dekker: New York, 2002; Chapter 3, pp 57−101.
(80) Gutsche, C. D. *Org. React. (NY)* **1954**, *8*, 364−429.
(81) Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100−3109.
(82) Padwa, A.; Stull, P. D. *Tetrahedron Lett.* **1987**, *28*, 5407−5410.
(83) Padwa, A.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 2037−2038.
(84) Padwa, A.; Chinn, R. L.; Hornbuckle, S. F.; Zhi, L. *Tetrahedron Lett.* **1989**, *30*, 301−304.
(85) Hodgson, D. M.; Stupple, P. A.; Johnstone, C. *Tetrahedron Lett.* **1997**, *38*, 6471−6472.
(86) Hodgson, D. M.; Stupple, P. A.; Johnstone, C. *Chem. Commun. (Cambridge, U. K.)* **1999**, 2185−2186.
(87) Hodgson, D. M.; Labande, A. H.; Pierard, F. Y. T. M.; Expósito Castro, M. A. *J. Org. Chem.* **2003**, *68*, 6153−6159.
(88) Kitagaki, S.; Yasugahira, M.; Anada, M.; Nakajima, M.; Hashimoto, S. *Tetrahedron Lett.* **2000**, *41*, 5931−5935.
(89) Suga, H.; Inoue, S.; Kakehi, A.; Shiro, M. *J. Org. Chem.* **2005**, *70*, 47−56.
(90) García Ruano, J. L.; Fraile, A.; Martín, M. R.; Núñez, A. *J. Org. Chem.* **2006**, *71*, 6536−6541.
(91) de March, P.; Huisgen, R. *J. Am. Chem. Soc.* **1982**, *104*, 4952.
(92) Huisgen, R.; de March, P. *J. Am. Chem. Soc.* **1982**, *104*, 4953−4954.
(93) Gill, H. S.; Landgrebe, J. A. *J. Org. Chem.* **1983**, *48*, 1051−1055.
(94) Ibata, T.; Liu, M. T. H.; Toyoda, J. *Tetrahedron Lett.* **1986**, *27*, 4383−4386.
(95) L'Esperance, R. P.; Ford, T. M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 209−213.
(96) Rosenberg, M. G.; Brinker, U. H. *J. Org. Chem.* **2003**, *68*, 4819−4832 ; see Supporting Information.
(97) Mendez, F.; Garcia-Garibay, M. A. *J. Org. Chem.* **1990**, *64*, 7061−7066.
(98) Brinker, U. H.; Bespokoev, A. A.; Reisenauer, H. P.; Schreiner, P. R. *J. Org. Chem.* **2012**, *77*, 3800−3807.
(99) Plazuk, D.; Warkentin, J.; Werstiuk, N. H. *Tetrahedron* **2005**, *61*, 5788−5796.
(100) Czardybon, W.; Warkentin, J.; Werstiuk, N. H. *Can. J. Chem.* **2003**, *81*, 1438−1442.
(101) Warkentin, J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2161−2169.
(102) Pezacki, J. P.; Loncke, P. G.; Ross, J. P.; Warkentin, J.; Gadosy, T. A. *Org. Lett.* **2000**, *2*, 2733−2736.
(103) Pezacki, J. P.; Couture, P.; Dunn, J. A.; Warkentin, J.; Wood, P. D.; Lusztyk, J.; Ford, F.; Platz, M. S. *J. Org. Chem.* **1999**, *64*, 4456−4464.
(104) Tae, E. L.; Zhu, Z.; Platz, M. S.; Pezacki, J. P.; Warkentin, J. *J. Phys. Chem. A* **1999**, *103*, 5336−5342.
(105) Pezacki, J. P.; Wood, P. D.; Gadosy, T. A.; Lusztyk, J.; Warkentin, J. *J. Am. Chem. Soc.* **1998**, *120*, 8681−8691.
(106) Pezacki, J. P.; Pole, D. L.; Warkentin, J. *J. Am. Chem. Soc.* **1997**, *119*, 3191−3192.
(107) Sharma, P. K.; Warkentin, J. *Tetrahedron Lett.* **1995**, *36*, 7591−7594.
(108) Kassam, K.; Warkentin, J. *J. Org. Chem.* **1994**, *59*, 5071−5075.
(109) Kassam, K.; Pole, D. L.; El-Saidi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1994**, *116*, 1161−1162.
(110) El-Saidi, M.; Kassam, K.; Pole, D. L.; Tadey, T.; Warkentin, J. *J. Am. Chem. Soc.* **1992**, *114*, 8751−8752.
(111) Békhazi, M.; Lawrynowicz, W.; Warkentin, J. *Can. J. Chem.* **1991**, *69*, 1507−1510.
(112) Békhazi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1983**, *105*, 1289−1292.
(113) Bekhazi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1981**, *103*, 2473−2474.
(114) Warkentin, J. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI: Stamford, CT, 1998; Vol. 2, pp 245−295.
(115) Warkentin, J. *Acc. Chem. Res.* **2009**, *42*, 205−212.
(116) Fittig, R. *Ann. Chem. Pharm.* **1860**, *114*, 54−63.
(117) Berson, J. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4655−4660.
(118) Jones, M., Jr.; Moss, R. A. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley-Interscience: Hoboken, NJ, 2004; Chapter 7, p 288.
(119) Moss, R. A.; Lawrynowicz, W.; Turro, N. J.; Gould, I. R.; Cha, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7028−7032.
(120) Moss, R. A.; Wang, L.; Zhang, M.; Skalit, C.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **2008**, *130*, 5634−5635.
(121) Moss, R. A.; Wang, L.; Krogh-Jespersen, K. *J. Org. Chem.* **2013**, *78*, 11040−11044.
(122) Moss, R. A.; Cang, H.; Krogh-Jespersen, K. *Tetrahedron Lett.* **2014**, *55*, 4278−4280.
(123) Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 4293−4294.
(124) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555−1563.
(125) Nakamura, K.; Osamura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9112−9120.
(126) Jensen, P.; Bunker, P. R. *J. Chem. Phys.* **1988**, *89*, 1327−1332.
(127) Gronert, S.; Keefe, J. R.; More O'Ferall, R. A. In *Contemporary Carbene Chemistry*; Moss, R. A., Doyle, M. P., Eds.; Wiley: Hoboken, NJ, 2014; Chapter 1, pp 3−39.
(128) Brinker, U. H.; Lin, G.; Xu, L.; Smith, W. B.; Mieusset, J.-L. *J. Org. Chem.* **2007**, *72*, 8434−8451.
(129) O'Donoghue, A. C.; Massey, R. S. In *Contemporary Carbene Chemistry*; Moss, R. A., Doyle, M. P., Eds.; Wiley: Hoboken, NJ, 2014; Chapter 3, pp 75−106.
(130) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734−740.
(131) Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 1999; p 176.
(132) Becker, R. S.; Bost, R. O.; Kolc, J.; Bertoniere, N. R.; Smith, R. L.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1302−1311.
(133) Thap, D.-M.; Trozzolo, A. M.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1402−1403.

(134) Griffin, G. W.; Bertoniere, N. R. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol *1*, Chapter 3, pp 318−332.
(135) Dawid, M.; Warkentin, J. *Can. J. Chem.* **2003**, *81*, 598−606.
(136) Dawid, M.; Venneri, P. C.; Warkentin, J. *Can. J. Chem.* **2001**, *79*, 110−113.
(137) Venneri, P. C.; Warkentin, J. *Can. J. Chem.* **2000**, *78*, 1194−1203.
(138) Scholz, F.; Himmel, D.; Heinemann, F. W.; Schleyer, P. v. R.; Meyer, K.; Krossing, I. *Science* **2013**, *341*, 62−64.
(139) Sargent, G. D. In *Carbonium Ions: Major Types (Continued)*; Olah, G. A., Schleyer, P. v. R., Eds.; Reactive Intermediates in Organic Chemistry; Wiley-Interscience: New York, 1972; Vol. *3*, Chapter 24, pp 1099−1200.
(140) Bartlett, P. D. *Nonclassical Carbonium Ions*; W. A. Benjamin: Menlo Park, CA, 1965.
(141) Berson, J. A. In *Molecular Rearrangements*; de Mayo, P., Ed.; Wiley-Interscience: New York, 1963; Part 1, Chapter 3, pp 111−231.
(142) Breslow, R. In *Molecular Rearrangements*; de Mayo, P., Ed.; Wiley-Interscience: New York, 1963; Part 1, Chapter 4, pp 233−294.
(143) Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808−820.
(144) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41−52.
(145) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432−440.
(146) Olah, G. A.; Surya Prakash, G. K.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440−448.
(147) Walling, C. *Acc. Chem. Res.* **1983**, *16*, 448−454.
(148) Brookhart, M.; Diaz, A.; Winstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 3135−3136.
(149) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183−4184.
(150) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1949**, *71*, 2953.
(151) Rzepa, H. S.; Allan, C. S. M. *J. Chem. Educ.* **2010**, *87*, 221−228.
(152) Creary, X.; Heffron, A. *J. Org. Chem.* **2014**, *79*, 2547−2555.
(153) Knoll, W.; Kaneno, D.; Bobek, M. M.; Brecker, L.; Rosenberg, M. G.; Tomoda, S.; Brinker, U. H. *J. Org. Chem.* **2012**, *77*, 1340−1360.
(154) Zhu, Y.; Shu, L.; Tu, Y.; Shi, Y. *J. Org. Chem.* **2001**, *66*, 1818−1826.
(155) Williams, J. R.; Sarkisian, G. M.; Quigley, J.; Hasiuk, A.; VanderVennen, R. *J. Org. Chem.* **1974**, *39*, 1028−1032.
(156) Kretchmer, R. A.; Frazee, W. J. *J. Org. Chem.* **1971**, *36*, 2855−2859.
(157) Hoffmann, R. W.; Luthardt, H. J. *Chem. Ber.* **1968**, *101*, 3861−3871.
(158) Williamson, K. L.; Coburn, J. I.; Herr, M. F. *J. Org. Chem.* **1967**, *32*, 3934−3937.
(159) Johnson, C. K.; Dominy, B.; Reusch, W. *J. Am. Chem. Soc.* **1963**, *85*, 3894−3896.
(160) Bly, R. K.; Bly, R. S. *J. Org. Chem.* **1963**, *28*, 3165−3172.
(161) Williamson, K. L.; Johnson, W. S. *J. Org. Chem.* **1961**, *26*, 4563−4569.
(162) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737−799.
(163) A group's migratory aptitude depends mainly on three factors: (i) the intrinsic migratory aptitude, (ii) the bystander substituent at the migration origin, and (iii) the spectator substituent at the migration terminus. For reviews, see (a) Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84−89. (b) Merrer, D. C.; Moss, R. A. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Elsevier: Amsterdam, 2001; Vol. *3*, pp 53−113.
(164) Smith, M. B.; March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed.; Wiley: New York, 2001; p 732.
(165) *Spartan'14 Parallel Suite,* version 1.1.8; Wavefunction Inc.: Irvine, CA, 2013.
(166) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(167) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789.
(168) Hehre, W. J. *A Guide to Molecular Mechanics and Quantum Chemical Calculations*; Wavefunction Inc.: Irvine, CA, 2003.
(169) Csonka, G. I.; Ruzsinszky, A.; Perdew, J. P. *J. Phys. Chem. A* **2005**, *109*, 6779−6789.
(170) (a) Frequency Scale Factors for ZPVE, $\Delta H_{\text{vib}}(T)$, and $S_{\text{vib}}(T)$. Radom Group Scale Factors. http://groups.chem.usyd.edu.au/radom/More/ScaleFactor.html (accessed July 12, 2015). (b) Merrick, J. P.; Moran, D.; Radom, L. *J. Phys. Chem. A* **2007**, *111*, 11683−11700. (c) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.