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Phenylhydroxycarbene

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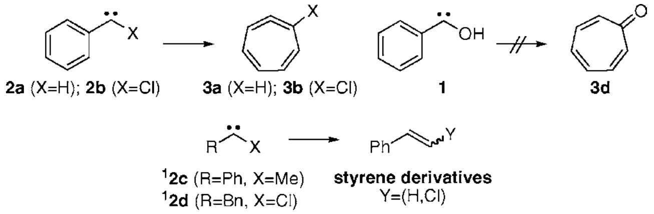
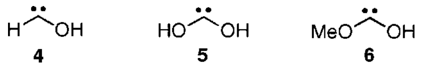
Phenylhydroxycarbene (**1**) is a hitherto unobserved π-donor-substituted singlet carbene of the recently discovered hydroxycarbene family.[1] The intermediacy of **1** in thermal rearrangements of hydroxyphenylcarbenes has been proposed.[2] Structure **1** bears resemblance to phenylcarbene (**2a**), phenylchlorocarbene (**2b**), and phenylmethylcarbene (**2c**). Carbene **2b** was first generated 50 years ago by base-induced hydrogen chloride elimination from benzal chloride;[3] **2a** was produced shortly thereafter by thermal extrusion of nitrogen from phenyldiazomethane,[4] and **2c** was obtained similarly to **2a**.[5] Various thermolyses, photolyses, and mass spectrometric studies followed,[6] uncovering the intriguing singlet-surface rearrangements of **2a** and **2b** to cyclohepta-1,2,4,6-tetraene (**3a**) and chlorocyclohepta-1,2,4,6-tetraene (**3b**), respectively (Scheme 1). Singlet carbenes ^{1}**2c** and ^{1}**2d**, on the other hand, produce styrene derivatives[7] as a result of small barriers (∼5 kcal mol^{-1})[8] for the thermal [1,2] H-shifts, whose rates are likely to include tunneling contributions.[7c] As demonstrated here, **1** does not undergo ring expansion to hydroxycyclohepta-1,2,4,6-tetraene (**3c**) or its tropone tautomer **3d** but instead exhibits a strikingly different reactivity.

Scheme 1. Reactivities of Some Arylcarbene Derivatives



Building on our recent breakthroughs in preparing the first members of the hydroxycarbene family, hydroxymethylene (**4**),[1] dihydroxycarbene (**5**),[9] and methoxyhydroxycarbene (**6**)[9] (Scheme 2), we sought to prepare **1**, the parent of all arylhydroxycarbenes. Remarkably, **4** shows rapid (within 2 h at 10 K) H-tunneling through a very large barrier (∼30 kcal mol^{-1})[1] to form formaldehyde, while neither **5** nor **6** disappears through such a process, despite comparable [1,2] H-shift barriers. Hence, we were particularly interested in the possible H-tunneling of **1** to yield benzaldehyde (**8**), a phenomenon that would also affect its higher-temperature behavior.

Scheme 2. Presently Characterized Members of the Hydroxycarbene Family



The thermal decarboxylation of α-ketocarboxylic acids has proved to be a versatile and reliable method for the generation of hydroxycarbenes.[1,9] Thus, we prepared the *s*-trans carbene **1t** and its monodeuterated analogue Ph−C−OD (*d*-**1t**) by decarboxylation of phenylglyoxylic acid (**7**) and d_1-phenylglyoxylic acid (*d*-**7**) through high-vacuum flash pyrolysis (HVFP) at 600 °C and instant trapping in an argon matrix at 11 K (Scheme 3). In order to identify all of the remaining signals of the starting material, **7** was evaporated and matrix-isolated without pyrolysis for comparison. Although the IR signals of carbenes **1t** and *d*-**1t** were rather weak, all of the characteristic absorptions of the hydroxycarbene moiety could be identified unambiguously by precise matching with anharmonic frequencies computed at a high level of theory (Table 1).

Scheme 3. Generation and Tunneling of Phenylhydroxycarbene

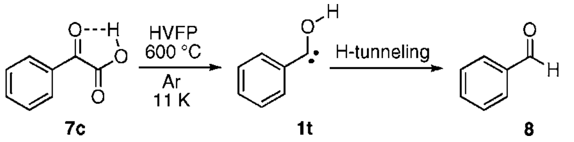


Table 1. Observed Vibrational Band Origins (cm^{-1}) of **1t** and *d*-**1t** and Precise Matching with Computed Values; Theoretical Absolute IR Intensities (Double-Harmonic, km mol^{-1}) and Experimental Relative Intensities Are Given in Parentheses

normal mode TED (%)[a]	symmetry	ν_{theor}[b]	ν_{expt}
Ph−C−OH (**1t**)			
OH stretch (100)	a′	3575 (166)	3570 (s)
HOC bend (50)	a′	1332 (27)	1334 (m)
CC stretch/ring breathing (60)	a′	1310 (26)	} 1297 (m)
HCC in-plane bends (56)	a′	1289 (76)	
CO stretch (53)	a′	1236 (218)	1219 (s)
HOCC torsion (82)	a″	800 (99)	} 800 (m)
carbene CC stretch (27)	a′	793 (24)	
ring def (66) − CCO bend (26)	a′	606 (12)	} 613 (w)
ring def (59) + CCO bend (17)	a′	606 (9)	
Ph−C−OD (*d*-**1t**)			
OD stretch (100)	a′	2645 (97)	2641 (s)
HCC in-plane bends (79)	a′	1297 (20)	1297 (w)
CO stretch (67)	a′	1258 (313)	1256 (s)
HCC in-plane bends (77)	a′	1159 (11)	1171 (m)
DOC bend (62)	a′	994 (33)	990 (m)
carbene CC stretch (25)	a′	760 (26)	770 (m)
HCC out-of-plane bends (87)	a″	750 (74)	765 (m)
ring def, out-of-plane (65)	a″	610 (19)	} 595 (w)
CCO bend (41)	a′	588 (27)	

[a] Leading components of the total energy distribution (TED) of the normal-mode vibrations.[10] [b] (Unscaled) anharmonic fundamental frequencies computed by applying second-order vibrational perturbation theory (VPT2)[11] (resonance cutoff = 40 cm^{-1}) to a quartic force field in natural internal coordinates.[12] The force field was evaluated with the cc-pVDZ basis set[13] as follows: CCSD(T)[14] for (F_{ii}, F_{ij}, F_{iii}, F_{iiii}), MP2 for (F_{iij}, F_{ijk}, F_{iiij}, F_{iijj}, F_{iijk}), and F_{ijkl} set to 0. A complete tabulation of theoretical frequencies and isotopic shifts is given in the SI.

The identification of **1t** was complicated by the presence of precursor conformer **7t** (*s*-trans, nonplanar, non-hydrogen-bridged)

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and its conversion to the lower-energy form **7c** (*s-cis*, planar, hydrogen-bridged) despite the cryogenic conditions, causing significant temporal changes in the IR intensities. This process was elucidated by enriching isomer **7t** via 313 nm irradiation. The measured first-order-decay half-life of **7t** was $\tau = 2.72$ h ± 18 min at 11 K and $\tau = 1.65$ h ± 4 min at 20 K. It is likely that the interconversion of **7t** to **7c** involves tunneling, as observed for the conformers of formic acid[15] and acetic acid.[16]

Irradiation at 546 nm of the matrix containing **1t** led to the disappearance of the carbene IR signals and an increase in the intensities of the aldehyde in the IR difference spectrum (shown in Figure 1 for *d*-**1t** and *d*-**8**). The complete absence of **3d** was verified with a matrix-isolated reference spectrum of **3d** under the same conditions [see the Supporting Information (SI)]. Tropone **3d** also proved to be resistant to HVFP conditions, and its intermediacy in the reactions of **1** can be ruled out.

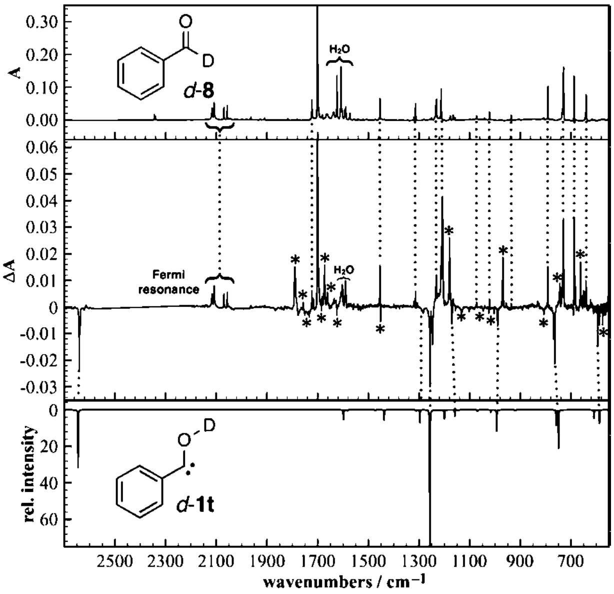


Figure 1. Experimental IR difference spectrum of the products of *d*-**7** pyrolysis at 600 °C instantly trapped in Ar at 11 K (center panel); absorption differences were taken after irradiation at 546 nm for 34 h. The assignments were established by anharmonic CCSD(T)/cc-pVDZ frequency computations for *d*-**1t** (bottom panel) and the experimental reference spectrum of *d*-**8** (top panel). Asterisks label remaining *d*-**7** bands, CO_2 (663 cm^{-1}), or measurement artifacts. The main CO_2 signal near 2343 cm^{-1} was cut for clarity. Detailed spectra of the parent **1t** are given in the SI.

Despite low extinction coefficients, UV−vis difference spectra of **1t** and *d*-**1t** were successfully recorded (Figure 2). These spectra display a broad band with maximum absorption at 500 ± 25 nm (2.5 ± 0.1 eV) that extends to ~640 nm (1.9 eV). A similar spectrum was observed previously for **4**.[1] The associated $S_0(^1A')$ → $S_1(^1A'')$ electronic transition, which induces decay of **1t** and conversion to **8**, arises from an excitation from the HOMO localized on the carbene moiety (Figure 2 inset). Our spectral assignments were confirmed unequivocally by a series of careful electronic structure computations that arrived at a gas-phase vertical (adiabatic) excitation energy of 2.7 (1.9) eV for **1t**, with an uncertainty of less than 0.1 eV. To maximize accuracy, these computations were dissected into a $S_0(^1A')$ → $T_1(^3A'')$ step treated by ROCCSD(T) theory[17] and a $T_1(^3A'')$ → $S_1(^1A'')$ step handled with the EOM-CCSD method,[18] applying high-quality cc-pVQZ and cc-pVTZ basis sets,[13] respectively. Moreover, an isogyric procedure (see the SI) was employed using H−C−F as a reference with a precisely known adiabatic excitation energy.

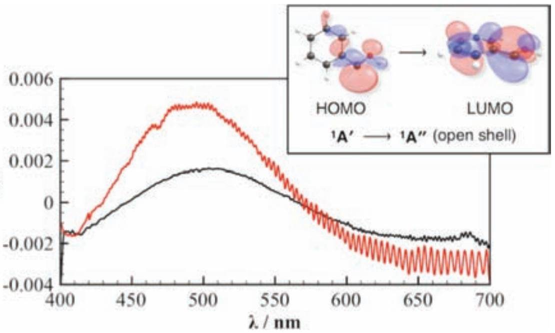
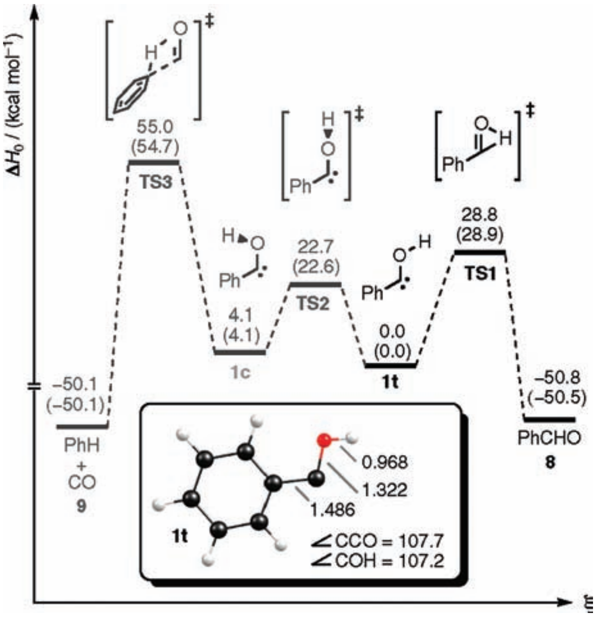


Figure 2. Experimental UV−vis difference spectra of **1t** (black) and *d*-**1t** (red) based on absorption changes after 19 h in the dark and 34 h of irradiation at 546 nm, respectively. The black curve, but not the red one, showed time dependence due to H-tunneling (see the SI). Inset: M06-2X/cc-pVDZ computed MOs of the corresponding electronic transition.

The key stationary points on the potential energy hypersurface (PES) of **1** were optimized at the M06-2X/cc-pVDZ level;[19] very similar structures were obtained from MP2/cc-pVDZ computations (see the SI).[20] M06-2X is an economical method that performs well for thermochemistry and reaction barriers[21] within systems composed of main-group elements. Certainty in the final energetics was ensured by rigorous CCSD(T)/cc-pVQZ single-point computations with auxiliary core correlation corrections, as reported in Scheme 4.

Scheme 4. Schematic PES Surrounding **1t**[a]



[a] Computed using CCSD(T)/cc-pVQZ single-point energies with (without) CCSD(T)/cc-pCVTZ[22] core correlation corrections and employing M06-2X/cc-pVDZ optimized geometries and zero-point vibrational energies (ZPVEs). The lowest triplet structure of **1** is 22.3 kcal mol^{-1} above **1t** at the same level. Selected M06-2X/cc-pVDZ bond lengths and angles are given in Å and deg, respectively; full geometric structures are provided in the SI. In contrast to **1t**, **1c** is nonplanar.

Structure **1t** lies 50.8 kcal mol^{-1} above **8**, but the corresponding [1,2] H-shift barrier is large (28.8 kcal mol^{-1}, **TS1**). The isomerization of **1t** to **1c** is blocked by a 22.7 kcal mol^{-1} barrier (**TS2**), while a very high-lying transition state (**TS3**) prevents access to the benzene + CO (**9**) products. The features of the PES are very favorable for the isolation of **1t**, as **1c**, **8**, and **9** are completely inaccessible by thermal activation under matrix conditions. The facile [1,2] H-shift in **2c** is not operative by thermal activation of **1t**. In addition, we found no evidence that **1t** undergoes the ring expansion reactions that occur for **2a** (photochemically or thermally)[6] and **2b** (photochemically).[6]

A reactivity previously undiscovered in the class of phenylcarbenes is exhibited by **1t**, even at the low temperatures of our experiments. Close monitoring of the major IR bands at 3570, 1334, 1297, 1219, and 800 cm^{-1} revealed that **1t** decays under matrix isolation with half-lives (τ) of 2.46 h ± 8 min at 11 K and 2.55 h ± 8 min at 20 K; Figure 3 displays representative measurements. In stark contrast, when *d*-**1t** signals were monitored, no changes were detected, even after 96 h in the dark at 20 K. The dramatic isotopic dependence and temperature insensitivity of the disappearance of **1t**, as well as the observation of concomitant increases in signals due to **8**, indicates that a quantum-mechanical tunneling mechanism is at work to engender a remarkable [1,2] H-shift.

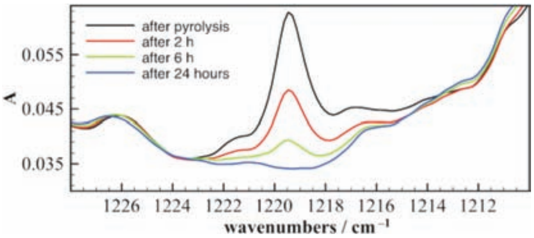


Figure 3. Disappearance of the IR band of **1t** at 1219 cm^{-1}.

To prove that the formidable 28.8 kcal mol^{-1} barrier separating **1t** from **8** does not preclude rapid H-tunneling even at 0 K, we executed the same type of theoretical analysis (detailed in the SI) that previously documented such a fascinating phenomenon for parent compound **4**.[1] The MP2/aug-cc-pVDZ method was used to precisely map out the intrinsic reaction path (IRP) connecting **TS1** to **1t** and **8**. A final potential energy curve along the isomerization IRP was then constructed from CCSD(T)/aug-cc-pVTZ[23] energy points and MP2/aug-cc-pVDZ[23] ZPVEs. Tunneling probabilities were evaluated by numerically computing one-dimensional barrier penetration integrals along the IRP and invoking the standard Wentzel−Kramers−Brillouin (WKB) formula.[24] A vibrational "reaction" mode of **1t** was identified leading toward **TS1** with a harmonic frequency (ω_0) of 1358 cm^{-1} was identified. The tunneling lifetime of **1t** near 0 K was then obtained by setting the "collision" energy (ε) equal to the ZPVE of the reaction mode ($\omega_0/2$), computing the WKB transmission coefficient at this energy [$\kappa(\varepsilon)$], and multiplying by the classical rate (ω_0) at which the reactant hits the barrier. This analysis yielded a half-life of $\tau = 3.3$ h for **1t** in its ground vibrational state, in excellent accord with experiment. The same procedure gave $\tau = 8700$ years for *d*-**1t**, confirming our matrix observation that *d*-**1t** is extremely long-lived.

In conclusion, we have synthesized and characterized a new member of the hydroxycarbene family, phenylhydroxycarbene (**1t**), which has a rather unique reactivity. Carbene **1t** does not show signs of ring insertion reactions typical for other phenylcarbenes such as **2a** or **2b**. Upon irradiation, it does not undergo ring expansion but yields benzaldehyde (**8**) instead. However, neither photoexcitation nor thermal activation is necessary for the isomerization of **1t** because it undergoes rapid H-tunneling to **8** through a large barrier (nearly 30 kcal mol^{-1}) with a half-life of a few hours even at cryogenic temperatures. Our findings, together with the published evidence for heavy-atom tunneling in carbenes,[25] expands our view of the importance and generality of tunneling mechanisms in chemical reactions.

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Supporting Information Available: Spectra, geometries, PESs, kinetic plots, and experimental and theoretical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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