

The Phenylcarbyne Anion

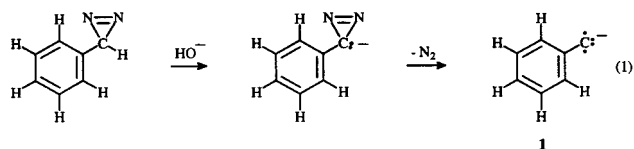
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Carbynes are highly reactive, monovalent carbon compounds of which only a handful of examples are known.¹ Like carbenes, they possess an open-valence shell with low-spin and high-spin states (doublets and quartets) that are relatively close in energy. Carbynes generally have doublet ground states with an sp(σ)-type lone pair, and one singly occupied and one empty p(π) orbital. Only for CH has the D–Q splitting been determined experimentally ($\Delta E_{DQ} = 17.1 \pm 0.2$ kcal/mol).² Experimental information about the negative ions of carbynes is also scarce, despite several compelling aspects of these species. Gaseous carbyne anions are required for measurements of carbyne D–Q splittings by negative ion photoelectron spectroscopy.³ Inasmuch as carbyne anions are isoelectronic with the corresponding neutral nitrenes, they may constitute a novel class of carbanions possessing *triplet ground states*. Moreover, the coordinative unsaturation of carbyne anions and their simultaneous resemblance to carbanions, carbenes and radicals make them attractive subjects for chemical reactivity studies. Herein we report the synthesis and structural characterization of phenylcarbyne anion **1**.

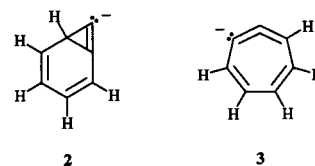
Phenyldiazirine⁴ reacts with OH[−] in a flowing afterglow triple-quadrupole apparatus⁵ to form phenyldiazirinylium anion⁶ and **1**, in a ca. 1:2 yield ratio (eq 1).



A key issue is whether ion **1** undergoes isomerization to either **2** or **3** since analogous rearrangements occur readily for isoelectronic phenylnitrene when it is generated in its singlet excited state.⁷ In fact, DFT calculations⁸ indicate that singlet carbanion **3** and ground-state triplet **1** (³A₂) are virtually isoenergetic, while **2** is ca. 7 kcal/mol higher in energy. Moreover, the lowest singlet state of **1** (¹A₁) is predicted to lie only about 6 kcal/mol above the triplet state, and the highest barrier on the

Table 1. Products from Gas-Phase Reactions of Phenylcarbyne Anion (**1**) with Selected Compounds

compd	products	compd	products
CO ₂	[C ₆ H ₅ C + CO ₂] [−] C ₆ H ₅ CO [−] + CO C ₆ H ₅ [−] + 2CO	O ₂	e [−] + [C ₆ H ₅ C + O ₂] C ₆ H ₅ CO ₂ [−] C ₆ H ₅ O [−] + CO C ₆ H ₃ [−] + CO + H ₂ O
N ₂ O	no reaction	SO ₂	C ₆ H ₅ CO ₂ [−] + S C ₆ H ₅ SO [−] + CO C ₆ H ₅ O [−] + OCS C ₆ H ₅ [−] + CO + SO
OCS	[C ₆ H ₅ C + OCS] [−] C ₆ H ₅ CS [−] + CO	ND ₃	no reaction
CS ₂	[C ₆ H ₅ C + CS ₂] [−] C ₆ H ₅ CS [−] + CS	D ₂ O	C ₆ H _{5−n} D _n C [−] (n = 1–5)
NO	e [−] + [C ₆ H ₅ C + NO] CNO [−] + C ₆ H ₅	CH ₃ OD	C ₆ H _{5−n} D _n C [−] (n = 1–5)



singlet surface for **1** → **3** isomerization (via **2**) is calculated to be only 11 kcal/mol above triplet **1**. The intersystem crossing between the ³A₂ and ¹A₁ states of **1** required for rearrangement is expected to be fast, since it is spin–orbit allowed with a low-energy requirement.⁹

The reactions of **1** with a series of small molecules were examined (see Table 1).¹⁰ Of immediate structural significance is that most of the reactions yield products in which a single carbon atom is lost from **1**. For example, while most carbanions react with CO₂ exclusively by addition to form carboxylate ions,^{11a} **1** reacts rapidly with CO₂ (*k*^{II} = 4.4 × 10^{−10} cm³/s) to yield phenyl anion as the major product, along with lesser amounts of an adduct and an oxygen-abstraction product identified as the benzoyl anion. Furthermore, ion **1** reacts with OCS and CS₂ by both addition and S-atom abstraction, but does not react at all with N₂O (*k*^{II} < 10^{−13} cm³/s). These results are inconsistent with the structures **2** and **3** because the model ions cyclopropen-1-yl anion¹² and allenyl anion¹³ do not abstract S-atom from either OCS or CS₂, and the latter anion slowly reacts with N₂O by condensation-cleavage to yield diazo anions.¹¹

The reaction of **1** with SO₂ is truly remarkable. Most carbanions react with SO₂ by simple addition and/or electron transfer.^{14,15} However, **1** yields predominantly C₇H₅O₂[−], which was identified by energy-resolved CID to be benzoate ion (lesser amounts of

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(6) Energy-resolved collision-induced dissociation experiments were used to distinguish phenyldiazirinylium anion from phenyldiazomethyl anion, which was independently prepared from benzyl anion and N₂O.¹¹

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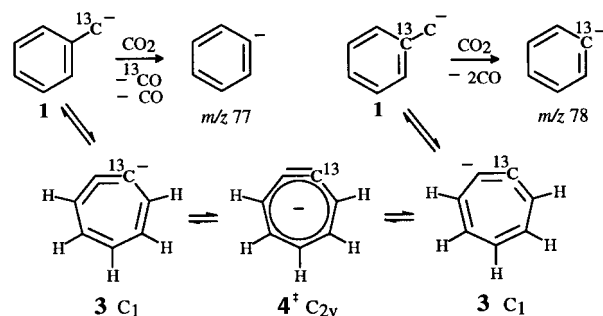
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phenyl anion, phenoxide, and an ion with the formula $C_6H_5OS^-$ are also observed [$k_{tot} = 1.7 \times 10^{-9} \text{ cm}^3/\text{s}$]. Elimination of a neutral sulfur atom in a negative ion/molecule reaction involving SO_2 is unprecedented.¹⁴ Nevertheless, the reduction of **1** with SO_2 is strongly exothermic ($\Delta H_{est} = -64 \text{ kcal/mol}$)¹⁶ due to the large energy release associated with forming a carboxylate group. Mechanistic details will be published elsewhere.¹⁷

Although the reactivity of the $C_7H_5^-$ ion toward most of the compounds is best interpreted in terms of the phenylcarbyne anion structure **1**,¹⁸ the acid–base behavior of this ion suggests a different conclusion. Bracketing experiments involving a series of reference acids give an apparent proton affinity (PA) for the $C_7H_5^-$ ion of $380.5 \pm 2.1 \text{ kcal/mol}$. In contrast, B3LYP/6-31+G(d) calculations carried out with an isodesmic reaction approach predict a PA of 370 kcal/mol for the triplet ground state **1**, while the computed PAs for the singlet ground states of **2** and **3** are 373 and 381 kcal/mol, respectively.¹⁹ This would seem to indicate that the observed $C_7H_5^-$ ion is isomer **3**. In addition, the $C_7H_5^-$ ion undergoes five rapid H/D exchanges in the presence of D_2O or CH_3OD , while it does not exchange at all with ND_3 . This behavior is readily explained with structure **3** but is inconsistent with **1**.²⁰ That is, the carbanion site in **1** is too weakly basic to undergo the initial D^+ abstraction from either D_2O ($\Delta H_{acid} = 392 \text{ kcal/mol}$) or ND_3 ($\Delta H_{acid} = 404 \text{ kcal/mol}$) that is necessary to initiate H/D exchange, while exchange with CH_3OD cannot occur since the PA of CH_3O^- is too small for subsequent abstraction of one of the ring hydrogens. In contrast, all of the hydrogens in **3** can become equivalent and exchangeable by a combination of reversible proton transfers and double bond shifts during collisions with the exchange agents.

What is the origin of this dual behavior? A static mixture of $C_7H_5^-$ isomers with differing reactivities is unlikely, since the reactions display pseudo-first-order kinetics, and can be carried out to completion. Moreover, the behavior of $C_7H_5^-$ toward CO_2 and SO_2 is unchanged by prior exposure to either H_2O or CH_3OH . We propose that **1** is the prevailing isomeric $C_7H_5^-$ form in the flow tube at equilibrium (it is slightly lower in energy than **3**), but it can be converted to **3** within an ion/molecule collision complex, provided enough internal energy is available from the ion/molecule interaction to surmount a small isomerization barrier. With the nonpolar and weakly polar aprotic reagents studied, the ion/molecule interaction energies ($<10 \text{ kcal/mol}$) are likely to be insufficient for **1** \rightarrow **3** isomerization. Thus, the observed reactivity appears to originate entirely from **1**. With polar, hydrogen-bonding molecules such as D_2O , CH_3OD , and the reference acids used in bracketing experiments, the larger ion/

Scheme 1



molecule interaction energies (ca. 15–20 kcal/mol) allow the rearrangement to take place within the ion/molecule complex, and the reactivity of **3** appears.

A ^{13}C -labeling experiment was designed to test this proposal. α - ^{13}C -Phenyldiazirine was used to prepare α - ^{13}C -phenylcarbyne anion via reaction (1). Reversible isomerization of **1** to **3** can lead to scrambling of the labeled α -carbon into the ipso position of the phenyl group of **1** (Scheme 1). Scrambling of the two dehydrocarbons in chiral ion **3** occurs by racemization via a planar C_{2v} transition state (**4**[‡]), 10 kcal/mol above **3** (B3LYP/aug-TZ). When a relatively acidic molecule such as water is present, additional carbon scrambling may occur by a combination of racemization (Scheme 1) and reversible proton transfers within the complex—these lead to H/D exchange with D_2O and CH_3OD . Since reaction of **1** with CO_2 leads to cleavage of the exocyclic carbon atom, the observed yields of $C_6H_5^-$ and ^{13}C - $C_6H_5^-$ can be used to evaluate the extent of label scrambling and, therefore, isomerization. Reaction of ^{13}C -**1** with CO_2 produces $C_6H_5^-$ and ^{13}C - $C_6H_5^-$ in a 3:1 yield ratio. Thus, some isomerization must be occurring during initial ion formation, although it is well-short of the statistical limit for complete C_{α}/C_{ipso} scrambling (1:1). This initial scrambling may be due to the excess internal energy gained by the phenylcarbyne anion upon formation,²¹ or it may be induced by the nascent H_2O molecule present in the ion/molecule complex when phenyldiazirine is deprotonated by OH^- . Reaction of ^{13}C -**1** with NH_3 prior to cleavage with CO_2 leads to a drop in the yield ratio to a value around 1:1. This finding indicates a complete C_{α}/C_{ipso} scrambling via the ring expansion/racemization mechanism (Scheme 1), which is consistent with the moderate polarity but low acidity of NH_3 ($\mu_D = 1.46D$; $\Delta H_{acid} = 404 \text{ kcal/mol}$), and the lack of H/D exchange with ND_3 . Reaction of ^{13}C -**1** with varying amounts of H_2O ($\mu_D = 1.8D$; $\Delta H_{acid}(H_2O) = 391 \text{ kcal/mol}$)¹⁶ prior to cleavage with CO_2 leads to a limiting value for the yield ratio of about 1:3 for the highest attainable flows of water. The ratio with H_2O catalyst is approaching the statistical limit of 1:6. This process requires reversible proton transfers within the intermediate ion–water complex via isomer **3**, and supports the view that the anomalous acid–base behavior of **1** arises from its facile skeletal rearrangement to **3** during collisions with polar molecules and Brønsted acids. Moreover, the persistence of characteristic phenylcarbyne anion reactivity following reactions with Brønsted acids requires that **1** is the prevailing isomeric form present at room temperature.

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(21) Using an estimated¹⁹ ΔH_f for phenyldiazirine (87 kcal/mol) and **1** (105 kcal/mol), we obtain an enthalpy change of -7 kcal/mol for formation of **1** by reaction 1.

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(18) It remains unclear whether the reactions occur from the 3A_2 or 1A_1 state of **1**. Given the computed ΔE_{ST} of 6 kcal/mol, it is possible that the 1A_1 state can be populated by the energy gained by complexation with the neutral molecule.

(19) For 3A_2 PhC^- , the PA was computed relative to the known value of $^3\Sigma^- CH^-$ (386.3 kcal/mol), while for **2** and **3** the PA was computed relative to the known PA of $CH_2=CH^-$ (409.4 kcal/mol). Cycloheptatetraene was the conjugate acid used to compute the PA of **3**.

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