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An Experimental and Computational Evaluation of the Energetics of the Isomeric Methoxyphenylcarbenes Generated in Carbon Atom Reactions

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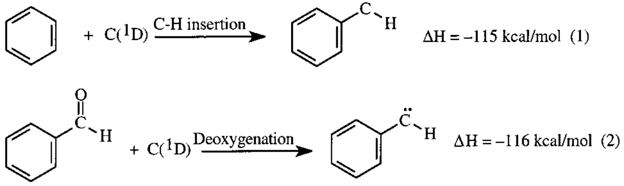
Abstract: Carbon atom reactions with anisole and methoxybenzaldehyde demonstrate the reversible ring expansion of methoxyphenylcarbene ($CH_3O-C_6H_4-C-H$). Trapping with HBF_4 yields the methoxytropylium ion, analogous to the well-known reactions of phenylcarbene. For instance, in the reaction of carbon atom with *p*-methoxybenzaldehyde, which proceeds by deoxygenation of the carbonyl group and formation of the corresponding arylcarbene, the products formed are methoxytropylium fluoroborate, *p*-methoxytoluene and *m*-methoxytoluene in yields of 69.4, 7.6, and 22.9%, respectively. Gas-phase density functional theory calculations were also carried out. The observed product yields from the uniquely generated *p*- and *m*-methoxyphenylcarbenes are in good agreement with the calculations. In the case of *o*-methoxyphenylcarbene, however, the calculations indicate that formation of dihydrobenzofuran is the most facile rearrangement on the *ground-state* singlet surface. In contrast, ring expansion is observed to be the major reaction path experimentally. The exothermicity of the deoxygenation step for carbon atom reaction with methoxybenzaldehyde (~100 kcal/mol) can allow for an excited singlet state to be formed initially. This excited singlet state of the methoxyphenylcarbene will resemble open-shell phenylnitrene, which is known to undergo ring expansion much more readily than phenylcarbene. On the basis of this analogy, we reconcile the difference in reactivity of the arylcarbene predicted by density functional theory calculations with the reactivity observed experimentally.

Introduction

Although carbenes are an extensively studied class of energetic intermediates,[1] investigations of their chemistry are often complicated by the fact that one must ensure that it is the reactions of the free carbene rather than those of an energetic precursor that are being studied.[2] This seems to be a particular problem in the case of nitrogenous carbene precursors (diazo compounds and diazirines) in which the precursor, either in its ground or excited state, also yields carbene-type products.[3] For this reason, it is often prudent to avoid the use of nitrogenous precursors and employ alternatives such as the cheleotropic extrusion of carbenes from cyclopropanes,[4] fragmentation reactions,[5] and gas-phase eliminations[6] or the formation of carbenes in carbon atom reactions.[7] However, each of these methods has its own potential drawbacks. As illustrated in eqs 1 and 2 for the formation of phenylcarbene, the reaction of atomic carbon with an organic substrate can lead to carbenes by several pathways including C−H insertion (eq 1) and deoxygenation of a carbonyl compound (eq 2).[8]



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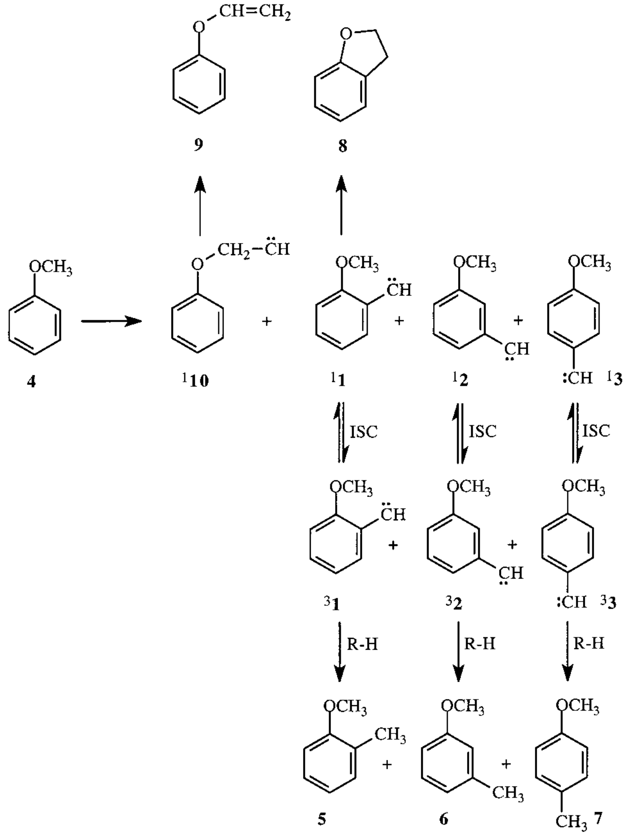
10.1021/ja012079t CCC: $22.00

Scheme 1. Proposed Mechanisms of Product Formation in the Reaction of C + **4**



Although these reactions are facile routes to carbenes, they differ from most other methods in that they involve highly exothermic reactions and would be expected to generate carbenes with a great deal of excess energy and perhaps yield chemistry different from carbenes with less internal energy. In fact, we have reported that the tolylcarbenes, generated by the C-atom deoxygenation of the corresponding tolylaldehydes, have sufficient energy to undergo the phenylcarbene rearrangement even when produced at 77 K.[9] We have also presented evidence for the formation of the first excited singlet state of methylene ($^1B_1$) in the deoxygenation of formaldehyde[10] and have recently reported an unusual fragmentation of cyclopentylidene generated in the deoxygenation of cyclopentanone.[11] This fragmentation, which proceeds in a stepwise manner, is certainly the result of excess energy in the carbene and may be that of an electronically excited singlet carbene.

These considerations make it important to assess the effect of excess energy on the chemistry of carbenes resulting from C-atom reactions. In this paper, we shall do this by generating the *o*-, *m*-, and *p*-methoxyphenylcarbenes ($CH_3O-C_6H_4-C-H$) **1**, **2**, and **3** (Scheme 1), by C-atom insertions and deoxygenations and comparing their reactivities with those predicted by computational techniques with density functional theory (DFT).[12]

Experimental Section

General Information. All ^{1}H and ^{13}C NMR were recorded on Bruker AM 250 or Bruker AM 400 spectrometers. Infrared spectra were obtained with an IR-44 IBM FT-IR. The GC/MS spectra were recorded on a Fisons Trios 2000 quadrupole spectrometer interfaced with a Hewlett-Packard Series II 5890 gas chromatograph equipped with a 30 m × 0.25 mm o.d. DB-5 column. Most of the chemicals were used as received from the Aldrich Chemical Co. The methoxybenzaldehydes were purified by forming bisulfite addition products from which the aldehydes were released by treatment with sodium carbonate solution. ^{13}C amorphous carbon was used as received from Isotec Inc.

Reaction of Atomic Carbon with Anisole (4). The carbon arc reactor was modeled after that described by Skell and co-workers.[13] Anisole (15.0 mmol) was condensed with atomic carbon at 77 K. When the reaction was over, the reactor was allowed to warm to room temperature, the contents were dissolved in ether and the solution was filtered and concentrated by rotary evaporation. The resulting products were analyzed by GC and GC/MS and compared with the authentic samples. Relative yields are shown in Table 1.

Reaction of Atomic Carbon with Anisole, Followed by the Addition of HBF$_4$. The reaction was carried out as described above by cocondensing **4** (15.0 mmol) with atomic carbon at 77 K. Before the reactor was allowed to warm, 1.0 mL of an ethereal solution of HBF_4 (7.3 mmol) was distilled into the reaction flask. The system was kept at 77 K for 0.5 h and then warmed to room temperature. All of the volatile substances were pumped to a U-trap and analyzed by GC (Table 1). The residue was extracted with acetonitrile. The extract was filtered, the solvent evaporated, and residue taken up in CD_3CN, and the resultant methoxytropylium fluoroborate (**11**, Figure 1) was analyzed by NMR: ^{1}H NMR (δ, ppm, CD_3CN) 8.76 (m, 2H, H_3), 8.59 (m, 2H, H_4), 8.44 (d, 2H, H_2); ^{13}C NMR (δ, ppm, CD_3CN) 182.7 (C_1), 152.7 (C_3), 149.1 (C_4), 139.8 (C_2), 61.7 (OCH_3).

Reaction of Atomic Carbon-13 with Anisole, Followed by the Addition of HBF$_4$. The reaction was carried out by cocondensing **4** (15.0 mmol) with ^{13}C-enriched carbon vapor at 77 K.[14] The resultant methoxytropylium fluoroborate (**11**) was analyzed by NMR. A comparison of the intensities of the ^{13}C NMR signals of methoxytropylium with those of methoxytropylium from the reaction of unlabeled carbon with **4** (taken under identical NMR conditions) revealed that the signals for C-2, C-3, and C-4 had increased by 30.9, 6.1, and 63.0%, respectively.

Reaction of Atomic Carbon with *o*-, *m*-, and *p*-Methoxybenzaldehyde (15−17), Followed by the Addition of HBF$_4$. 2-, 3-, or 4-methoxybenzaldehyde (**15**−**17**, 14.5 mmol) was cocondensed with atomic carbon at 77 K. Before the reactor was allowed to warm, 1.0 mL of an ethereal solution of HBF_4 (7.3 mmol) was distilled into the flask. The system was kept at 77 K for 0.5 h and then warmed to room temperature. All of the volatile substances were pumped to a 77 K U-trap and analyzed by GC. The residue was extracted with acetonitrile and filtered. The solvent was evaporated by rotary evaporation. The resulting products were analyzed by GC, GC/MS, and NMR (Table 1).

Reaction of Atomic Carbon with 1:1 mixture of *m*- and *p*-Methoxybenzaldehyde (16 and 17). A mixture of **16** and **17** (total 15.0 mmol) was condensed with atomic carbon at 77 K. When the

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Table 1. Products from Carbenes **1**−**3** Generated by C-Atom Reactions

	relative yield of products (%)								
reactants	**5**	**6**	**7**	**8**	**9**	**11**	**15**	**16**	**17**
C + **4**	29.6	14.5	18.9	6.6	30.4	a	*a*	*a*	*a*
C + **4** + HBF_4	11.1	9.3	4.2	12.7	37.1	25.5	*a*	*a*	*a*
C + **15** + HBF_4	9.5	15.2	*a*	13.9	*a*	61.5	*a*	*a*	*a*
C + **16** + HBF_4	*a*	60.8	6.0	*a*	*a*	33.2	*a*	*a*	*a*
C + **17** + HBF_4	*a*	22.9	7.6	*a*	*a*	69.4	*a*	*a*	*a*
C + **16** + **17**	2.1	77.9	14.0	6.0	*a*	*a*	*a*	*a*	*a*
C + **4** + O_2	7.7	27.1	2.5	2.8	10.7	*a*	5.7	41.5	2.1
C + **4** + O_2 + HBF_4	6.1	28.1	5.3	2.9	10.4	10.0	3.0	32.3	1.8
C + **4** + O_2[b]	13.9	30.8	22.5	6.6	21.3	*a*	1.7	2.0	1.3

[a] Not detected. [b]Oxygen added to the 77 K matrix after reaction.

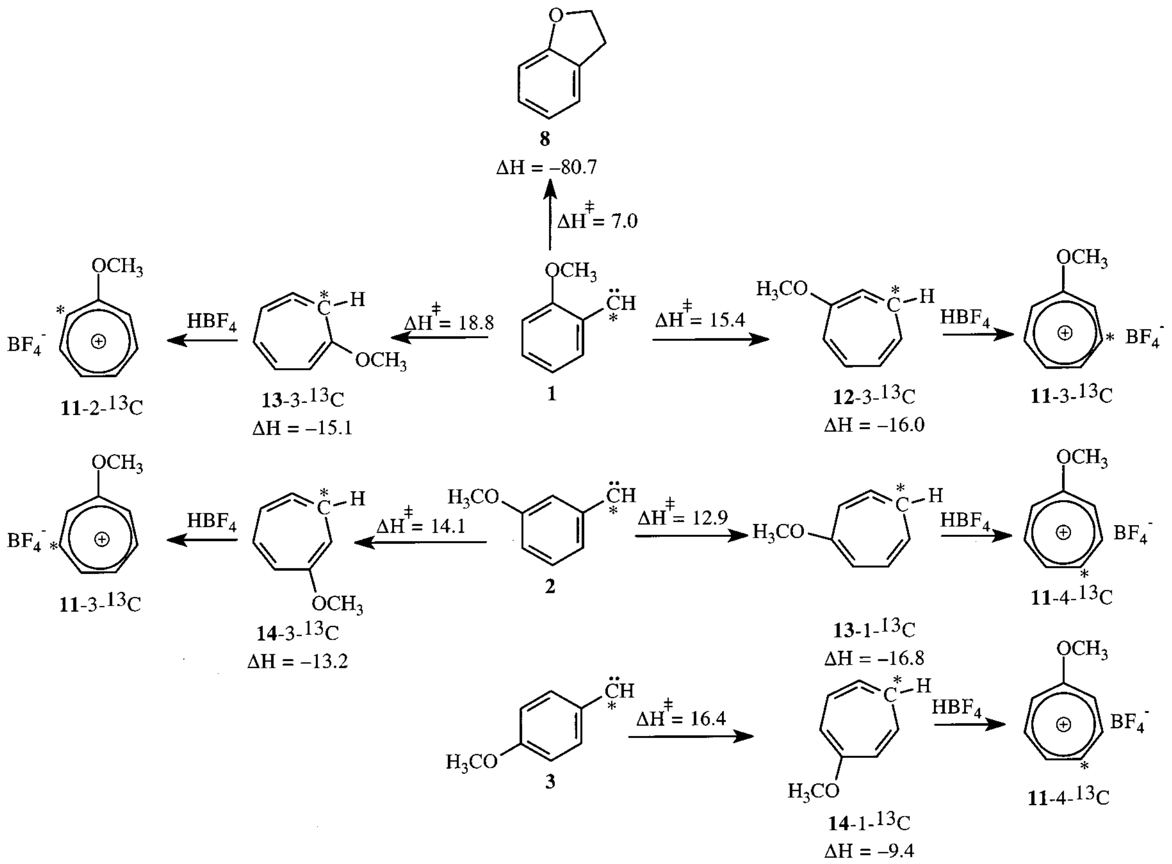

Figure 1. Fate of ^{13}C atoms undergoing reaction with **4** by C−H insertion to give carbenes **1**−**3**. Activation energies and heats of reaction (B3LYP/6-311+G**//B3LYP/6-31G*; kcal/mol) are given for singlets **1**−**3** from the lowest energy methoxy conformer of the carbene.

reaction was over, the reactor was allowed to warm to room temperature and extracted with ether. The extract was filtered and the solvent was concentrated by rotary evaporation. The resulting products were analyzed by GC, GC/MS, and NMR.

Reaction of Atomic Carbon with Anisole in the Presence of Oxygen. 4 (15.0 mmol) was distilled into the reactor together with O_2 (excess) and cocondensed with atomic carbon at 77 K. When the reaction was over, the reactor was allowed to warm to room temperature. The reaction was extracted with ether. The extract was filtered, and the solvent was concentrated by rotary evaporation. The resulting products were analyzed by GC and GC/MS and compared with the authentic samples (Table 1).

Reaction of Atomic Carbon with Anisole in the Presence of Oxygen, Followed by the Addition of HBF_4. 4 (15.0 mmol) was distilled into the reactor together with O_2 (excess) and cocondensed with atomic carbon at 77 K. Before the reactor was allowed to warm, 1.0 mL of an ethereal solution of HBF_4 (7.3 mmol) was distilled into the flask. The system was kept at 77 K for 0.5 h and then warmed to room temperature. All of the volatile substances were pumped to a 77 K U-trap and analyzed by GC. The residue was extracted with acetonitrile and filtered. The solvent was evaporated by rotary evaporation. The resulting products were analyzed by GC, GC/MS, and NMR (Table 1).

Computational Methods. The geometry of each stationary point was optimized using the three-parameter hybrid functional of Becke for exchange[15] and the gradient-corrected functional of Lee and coworkers for electron correlation[16] (B3LYP). The 6-31G* basis set[17] was used for these optimizations, and analytical second derivatives were computed to confirm each stationary point to be a minimum by yielding zero imaginary vibrational frequencies for the intermediates and one imaginary vibrational frequency for each transition state. These

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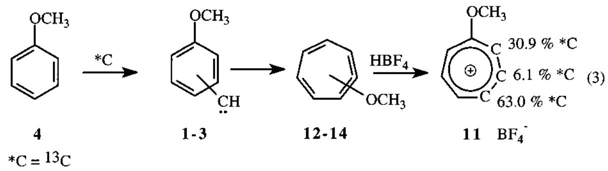
frequency analyses are known to overestimate the magnitude of the vibrational frequencies. Therefore, we scaled the corresponding zero-point vibrational energy (ZPE) corrections by 0.9806.[18] Single-point energy calculations were also carried with the B3LYP/6-311+G** level[17b] with six Cartesian d functions using the B3LYP/6-31G* geometries. The energies reported in the text will correspond to this single-point energy calculation (B3LYP/6-311+G**//B3LYP/6-31G*). All calculations were carried out with the Gaussian 98 suite[19] of programs. In this paper, the relative energy reported corresponds to ΔH_0, which includes the electronic energy of the molecule and the scaled zero-point vibrational energy correction obtained from the vibrational frequency analysis.

Results and Discussion

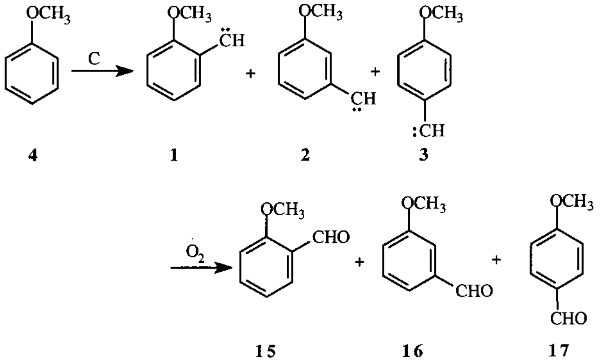
Reaction of Atomic Carbon with Anisole. Since there is evidence that singlet carbon atoms react with aromatic rings by C−H insertion to give phenylcarbenes,[14,20] the reaction of C(^{1}D) with **4** is expected to be a source of the *o*-, *m*-, and *p*-methoxyphenylcarbenes **1**−**3** (Scheme 1). Accordingly, we have reacted arc-generated carbon atoms with **4** at 77 K and have obtained the *o*-, *m*-, and *p*-methoxytoluenes, **5**−**7**, dihydrobenzofuran, **8**, and phenyl vinyl ether, **9**, in the ratios shown in Table 1. In Scheme 1, we have outlined the most reasonable routes to these products. Thus, insertion into a methoxy C−H bond generates phenoxyethylidene **10**, from which subsequent hydrogen migration produces **9**. An insertion into the *o*-, *m*-, and *p*-C−H bonds of anisole generates the isomeric methoxyphenylcarbenes **1**−**3**. These three singlet carbenes can undergo intersystem crossing (ISC) to their corresponding triplet states which can then abstract hydrogen from unreacted anisole to give the methoxytoluenes **5**−**7**. The *o*-methoxyphenylcarbene **1** has the additional ability to undergo intramolecular insertion into a methoxy C−H bond producing dihydrobenzofuran **8**.

While the reaction of C with **4** provides evidence for the intermediacy of carbenes **1**−**3**, it does not evaluate the extent of ring expansion to the corresponding methoxycycloheptatetraenes **12**−**14** (eq 3), a well-documented reaction of energetic phenylcarbenes.[21,22] We have been successful in trapping cycloheptatetraenes formed in the reaction of C with aromatic hydrocarbons by adding HBF_4 to the products at 77 K and isolating the corresponding tropylium fluoroborates.[14] In the present investigation, addition of HBF_4 to the 77 K matrix of C + **4** after reaction results in the formation of methoxytropylium fluoroborate **11** (eq 3) along with the previously mentioned products. When this reaction was carried out using carbon vapor enriched in ^{13}C, **11** with excess ^{13}C in the 2-, 3- and 4-positions (30.9, 6.1, and 63.0%, respectively) was formed (see Figure 1). The formation of **11** can be rationalized by proposing that carbenes **1**−**3** ring expand to the corresponding methoxycycloheptatetraenes **12**−**14**, which are then protonated by HBF_4 to give **11**.



(3)

Although it is reasonable to assume that **5**−**7** result from H abstraction by triplet **1**−**3**, another possible route to these isomeric methoxytoluenes would simply be insertion of CH_2, formed by H-atom abstraction by C, into the aromatic C−H bonds of **4**. To evaluate this possibility, we have added O_2 to the reactants as a trap for the triplet carbenes. This experiment, which results in trapping triplet **1**−**3** as the corresponding methoxybenzaldehydes **15**−**17** (eq 4, Table 1), indicates substantial formation of triplet **1**−**3** in this reaction.



(4)

Table 1 demonstrates that **16**, from trapping of triplet **3**, predominates in this reaction in both the presence and absence of HBF_4. The fact that total product yields do not decrease in the presence of O_2 indicates that C(^{3}P), which would be rapidly scavenged by oxygen, does not react with **4** to give **1**−**3**. The reaction must proceed instead from C(^{1}D). Addition of oxygen to the 77 K matrix after reaction between C and **4** does result in some **15**−**17** from reaction with carbenes **1**−**3** respectively.

Generation of the *o*-, *m*-, and *p*-Methoxyphenylcarbenes by Deoxygenation of the Corresponding Methoxybenzaldehydes. Although the trapping of **11** indicates that some of the methoxyphenylcarbenes ring-expand to the corresponding methoxycycloheptatetraenes **12**−**14**, it is possible that these products arise by C-atom addition to the π bonds of **4** followed by ring expansion. To evaluate this possibility, we have generated carbenes **1**−**3** by the deoxygenation of the corresponding *o*-, *m*-, and *p*-methoxybenzaldehydes **15**−**17**, a reaction that yields a distinct methoxyphenylcarbene intermediate and is comparable in exothermicity to the formation of **1**−**3** by initial C−H

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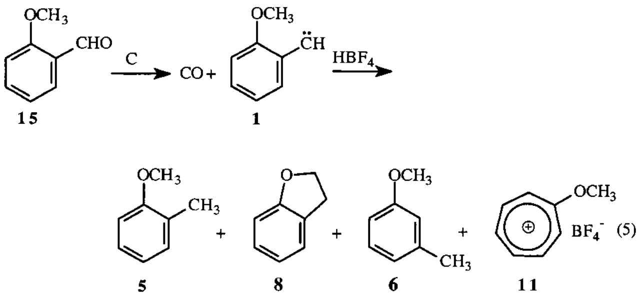
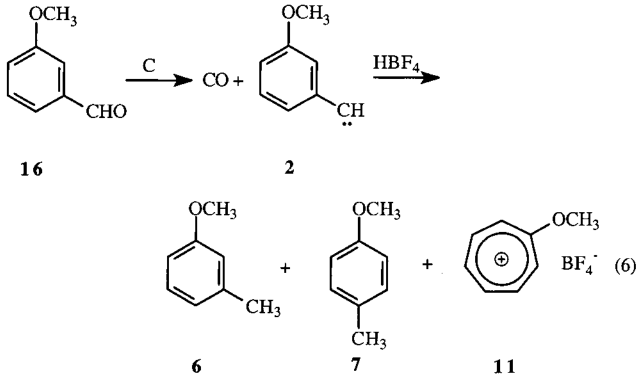
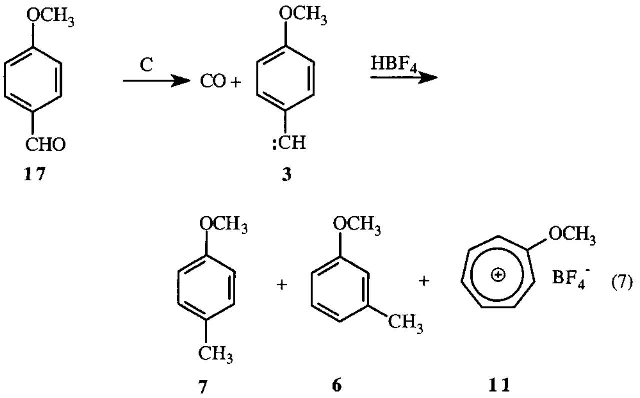
insertion.[8] The products of these reactions are shown in eqs 5−7, and their relative yields are provided in Table 1.







The fact that deoxygenation of aldehydes **15**−**17** also results in the formation of methoxytropylium ion **11** after the addition of HBF_4 to the low-temperature matrix provides convincing evidence that carbenes **1**−**3** have enough energy to ring-expand to the corresponding methoxycycloheptatetraenes under the reaction conditions. Furthermore, the observation of *o*-, *m*-, or *p*-methoxytoluene, which are triplet products, from each initially generated carbene isomer (for example, **6** from the deoxygenation of **17**) indicates that the ring-expansion process is reversible under the reaction conditions.

There are two general aspects of the chemistry of carbenes **1**−**3** that emerge from these experiments. The first concerns the spin states of **1**−**3**. Since both C-atom routes to **1**−**3** give products of both singlet and triplet carbenes, it is reasonable to conclude that both spin states are present and that the triplet is the ground state of **1**−**3**. This latter conclusion follows from the fact that the precursors of **1**−**3** are singlet carbon atoms and the initially formed singlet carbenes would not degrade to their triplets unless these were the ground states. It is interesting that generation of pure **1**, **2**, or **3** by deoxygenation of the corresponding aldehyde precursor always gives **6**, the H-atom abstraction product of triplet **2** (Scheme 1), as the highest yield triplet product. This behavior can be rationalized by assuming that **1**−**3** interconvert via their singlet states and also equilibrate with their respective triplet states. If it is further assumed that the singlet−triplet energy gap is largest in **2**, then this carbene will act as a quasi-thermodynamic sink and H-atom abstraction products from it will predominate. Thus, we deduce that carbenes **1**−**3** have triplet ground states and that the S−T gap is greatest in **2**. In fact, in a computational survey of substituted phenylcarbenes, two of us have reported that **1**−**3** have triplet ground states with S−T gaps of 3.3, 5.1, and 1.4 kcal/mol, respectively (Table 2).[23] Thus, the thermodynamics of carbenes **1**−**3**, which should be unaffected by the method of carbene generation, are accurately reflected in the chemistry of **1**−**3** generated in these experiments.

Table 2. Singlet−Triplet Energy Gap and Regioisomer Relative Energy for Methoxyphenylcarbenes (kcal/mol)[a,b]

regioisomer	ΔE_{ST}[c]	singlet relative energy[d]	triplet relative energy[e]
ortho	3.3	1.9	−0.1
meta	5.1	3.9	0.1
para	1.4	0.0	0.0

[a] Values taken from ref 23. [b] Values correspond to ΔH, 0 K calculated at the B3LYP/6-311+G**//B3LYP/6-31G* level of theory. [c] A positive value indicates that the triplet state is more stable than the singlet state. Values correspond to an energetic comparison of the most stable singlet and triplet species for each isomer. [d] Relative energies for the ortho and meta isomers are given relative to the para isomer, which is set at zero for the singlet states. [e] Relative energies for the ortho and meta isomers are given relative to the para isomer, which is set at zero for the triplet states.

A second aspect of these experiments concerns the chemistry of singlet **1**−**3.** The chemistry of singlet **2** and **3** proceeds as expected. These singlets either ring-expand to the corresponding methoxycycloheptatetraenes or decay to their triplet states. However, singlet **1** has two competing pathways available to it: intramolecular C−H insertion to produce **8** and ring expansion to either 1-methoxycycloheptatetraene **12** or 4-methoxycycloheptatetraene **13**. The experiments clearly indicate that carbene **1**, when generated by C-atom reactions, prefers to ring expand rather than undergo intramolecular C−H insertion. Since these are two competing reactions of singlet **1** that have easily calculable barriers, our observed chemistry of **1** can be compared to that calculated for **1** in which the energy has been equilibrated in a singlet ground state.

In the following section, we shall discuss the calculated energies of **1**−**3** in both singlet and triplet states and the reactivity profiles expected for the singlet cabenes.

Computational Study of Methoxyphenylcarbenes 1−3. The potential energy surface for the rearrangement of **1**−**3** is complicated by the number of unique rotational isomers arising from rotation about the C−C bond connecting the carbene to the phenyl ring and the C−O bond between the ring and the methoxy substituent. Since the regiochemistry of ring expansion is controlled by the conformation of the carbene, understanding the interconversion of conformers is vital to understanding the potential energy surfaces. We have therefore calculated the barrier to interconversion of the possible rotamers shown in Scheme 2. The energies for these interconversions as well as selected geometric parameters are presented for both the singlet (Table 3) and triplet (Table 4) carbenes.

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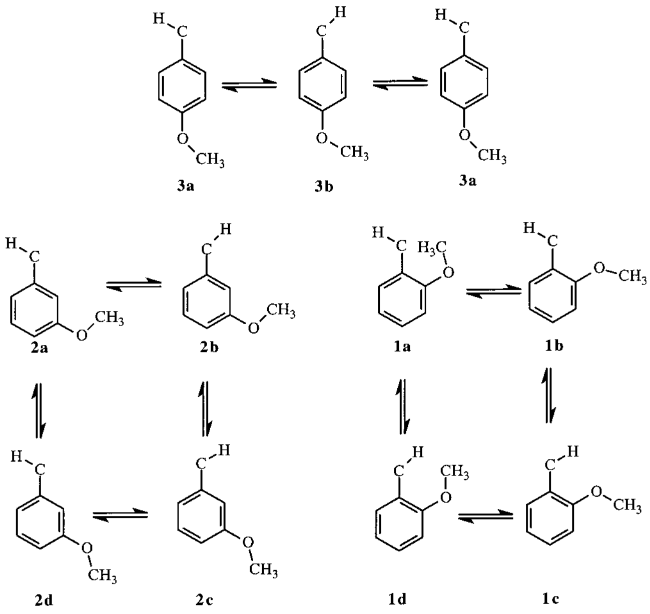
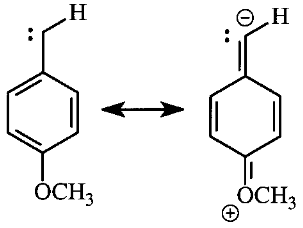
(23) Geise, C. M.; Hadad, C. M. *J. Org. Chem.* **2000**, *65*, 8348.

Scheme 2



The rotational barriers for singlet **1**−**3** about the ring carbene C−C bond are largest in the para isomer, **3** (Table 3). This is likely due to resonance interaction of the methoxy lone pairs with the empty p-type orbital on the carbene center, giving rise to the ylide resonance form shown below.



As expected from this model, the C−C rotational barrier calculated at the B3LYP/6-311+G**//B3LYP/6-31G* level (17.7 kcal/mol) is higher than the $\sim$11 kcal/mol barrier calculated for phenylcarbene.[24] Most importantly, the barrier to rotation about the C−O bond is only 5.3 kcal/mol. This will play a role in choosing which rotamers to use for comparison in the potential energy surfaces for rearrangement.

The meta isomers **2** have lower C−C rotational barriers than **3**, which further supports the resonance interaction explanation (Table 3). As well, the C−O bond rotations in **2** have activation barriers that are $\sim$2 kcal/mol lower than those in **3**, also in line with our resonance interaction picture. Again here, the C−O bond rotations have much lower activation energies than the C−C bond rotations. The rotations in the ortho isomers **1** are complicated by the steric interaction of the proximal substituent. Here, even though resonance interaction is possible, the C−C rotational barrier is only raised to 14.0 kcal/mol. Due to a combination of increased carbene energy (1.9 kcal/mol) owing to steric interactions with the ortho substituent (Table 2) and resonance conjugation with the carbene center, the rotational barrier is only slightly increased. Again, C−O bond rotation is much more facile than C−C bond rotation in the ortho isomers (difference in activation barriers $\geq$6.0 kcal/mol).

Bond rotation in the triplet carbenes has a lower activation barrier than singlet carbenes (Table 4 vis à vis Table 3). This is due to the decreased conjugation of the SOMO in triplets **1**−**3** with the aromatic ring compared to the empty p-type orbital of the singlet states. These results are presented in Table 4. We have calculated the potential energy surface for rearrangement of the singlet species only in this work, since it is likely that these rearrangements are much more facile than those of the triplet states.[25] Certainly, though, the triplet carbenes are involved in some of the chemistry in these experiments, as H-atom abstraction products **5**−**7** arising from the triplet carbenes are observed.

The relative energy of the intermediates involved in the reversible ring expansion and isomerization of **1**−**3** as well as the activation barriers separating them is presented in Figure 2 (also shown is the C−H insertion process that leads to dihydrobenzofuran **8**). The activation energy for the ring expansion (the rate-limiting step is formation of bicyclo[4.1.0]-(methoxy)hepta-2,4,6-trienes, **18**−**22**) is similar to that of C−C bond rotation in the singlet carbene. However, these activation barriers lie well above those for C−O bond rotation. We, therefore, assume that these reactions will proceed as predicted by the Curtin−Hammett principle.[26] Consequently, the energy reported for each stationary point (intermediate and transition state) corresponds to the methoxy rotamer with the lowest overall energy, but C−C carbene rotamers are treated as unique intermediates. The activation barriers here are given with respect to the intermediate from which they are formed.

Figure 3 shows the composite potential energy surface for the process described in Figure 2 (excluding rearrangement to **8**) with *p*-methoxyphenylcarbene (**3**) as the reference with an energy of 0.0 kcal/mol. The competitiveness of C−C bond rotation with ring expansion becomes even clearer when viewed graphically. 4-Methoxycycloheptatetraene (**12**) represents the global minimum in this ring-expansion process. Beginning with either carbene **2** or **3** (or anywhere else on the PES prior to **1** as shown in Figure 3), the ring contraction from **13** → **21** → **1** is the rate-limiting step in the rearrangement to the ortho isomer. This agrees well with the lack of formation of **8**, the global minimum on this potential energy surface, from **2** or **3** (for singlet rearrangement). However, formation of methoxytoluenes **7** and particularly **6** acts as a "sink" in the reaction of **2** and **3**; thus, no products derived from the reaction of **1** are observed when **2** and **3** are independently generated (Table 1). This is likely due to the greater stability of the triplet in **2** ($\Delta E_{\mathrm{ST}} = 5.1$ kcal/mol, Table 2), which leads to the formation of **6** as the major product from **2** and **3** (Table 1). The rearrangement pathway to form **8** is available only to **1**. Insertion of the carbene into a C−H bond of the methoxy group from the anti isomer to yield **8** is calculated to be exothermic by 80.7 kcal/mol (from

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(24) (a) Cramer, C. J.; Dulles, F. J. *J. Am. Chem. Soc.* **1994**, *116*, 9787. (b) Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 6942. (c) Kirmse, W.; Kund, K.; Ritzer, E.; Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1986**, *108*, 6045.

(25) Carbene intramolecular rearrangements are, in general, believed to take place primarily on the singlet surface; see: (a) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512. (b) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002. (c) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964. (d) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1964.

(26) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111. In Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970; p 120, Hammett refers to this as the "Curtin principle". Later, he says "because Curtin is very generous in attributing credit, this is sometimes referred to as the Curtin−Hammett principle."

Table 3. Relative Energy (ΔH, 0 K) of the Regioisomers of the Singlet Methoxyphenylcarbenes and the Rotational Transition States That Connect the Different Rotational Isomers

species[a]	comment	$\tau_{H-C-C-C}$[b]	$\tau_{C-O-C-C}$[b]	B3LYP/6-31G*[c,d]	B3LYP/6-311+G**//B3LYP/6-31G*[c,d]
3a		180.0	0.0	0.0	0.0
ts**3a**−**3b**	carbene rotation	92.3	0.1	16.8	17.7
3b		0.0	0.0	0.2	0.2
ts**3b**−**3a**	methoxy rotation	179.7	91.2	5.2	5.3
2a		180.0	0.0	0.0	0.0
ts**2a**−**2b**	carbene rotation	91.7	0.9	11.5	12.2
2b		0.0	0.0	0.3	0.4
ts**2b**−**2c**	methoxy rotation	1.9	93.0	3.3	3.4
2c		2.0	180.0	1.0	1.2
ts**2c**−**2d**	carbene rotation	92.4	179.9	11.4	12.1
2d		180.0	180.0	1.1	1.2
ts**2d**−**2a**	methoxy rotation	−179.6	102.4	3.3	3.4
1a		180.0	0.1	0.0	0.0
ts**1a**−**1b**	methoxy rotation	174.1	114.7	6.0	6.0
1b		176.5	178.5	3.5	2.9
ts**1b**−**1c**	carbene rotation	94.8	174.3	14.6	14.0
1c		0.0	180.0	1.0	0.4
ts**1c**−**1d**	methoxy rotation	5.4	92.5	5.1	4.4
1d		7.0	22.3	4.9	4.3
ts**1d**−**1a**	carbene rotation	*e*	*e*	*e*	*e*

[a] See Scheme 2 for structures. [b] Dihedral angles are in degrees. [c] Fully optimized structure at the B3LYP/6-31G* level of theory. [d] Relative energy is given in kcal/mol. [e] Rotation of the carbene out of plane in **1d** (or **1a**) is complicated by 1,5-H migration to give the bicyclic ether. This process has an activation barrier of 7.0 kcal/mol at the B3LYP/6-311+G**//B3LYP/6-31G* level of theory and is exothermic by 80.7 kcal/mol from **1d** → **8**.

Table 4. Relative Energy (ΔH, 0 K) of the Regioisomers of the Triplet Methoxyphenylcarbenes and the Rotational Transition States That Connect the Different Rotational Isomers

species[a]	comment	$\tau_{H-C-C-C}$[b]	$\tau_{C-O-C-C}$[b]	B3LYP/6-31G*[c,d]	B3LYP/6-311+G**//B3LYP/6-31G*[c,d]
3a		180.0	0.0	0.0	0.0
ts**3a**−**3b**	carbene rotation	91.4	−0.1	3.2	2.9
3b		0.0	0.0	0.0	0.0
ts**3b**−**3a**	methoxy rotation	0.0	90.8	2.8	2.8
2a		180.0	0.0	0.0	0.0
ts**2a**−**2b**	carbene rotation	91.1	−0.5	3.7	3.5
2b		0.0	0.0	0.2	0.2
ts**2b**−**2c**	methoxy rotation	−0.1	85.8	2.8	2.8
2c		0.0	180.0	0.6	0.7
ts**2c**−**2d**	carbene rotation	91.6	179.9	4.2	4.0
2d		180.0	180.0	0.6	0.6
ts**2d**−**2a**	methoxy rotation	179.8	88.3	2.8	2.8
1a		179.3	28.4	0.0	0.0
ts**1a**−**1b**	methoxy rotation	179.9	106.8	0.6	0.6
1b		180.0	180.0	−2.1	−2.1
ts**1b**−**1c**	carbene rotation	96.8	179.9	1.3	1.0
1c		0.0	180.0	−2.7	−2.8
ts**1c**−**1d**	methoxy rotation	*e*	*e*	*e*	*e*
1d		*e*	*e*	*e*	*e*
ts**1d**−**1a**	carbene rotation	*e*	*e*	*e*	*e*

[a] See Scheme 2 for structures. [b] Dihedral angles are in degrees. [c] Fully optimized structure at the B3LYP/6-31G* level of theory. [d] Relative energy is given in kcal/mol. [e] The triplet structure corresponding to **1d** is a rotational transition state connecting **1c** to itself.

anti-**1**) and has an activation barrier of only 7.0 kcal/mol. Therefore, we expect that this should be the major reaction channel for any *ground-state* singlet **1** formed in these reactions.

Relationship between Computational and Experimental Results. As indicated earlier, carbenes **1**−**3** are calculated to have triplet ground states with the S−T gap being the largest in **2** (Table 2). This rationalizes the experimental observation that these carbenes give triplet-derived reaction products which are dominated by products formed from the most stable triplet state (carbene ^{3}**2**) irrespective of which carbene is initially produced. Of course, the formation of products of triplet **2** when either **1** or **3** is generated requires that the carbenes interconvert under the reaction conditions. Since we have calculated that the barriers for these interconversions range from 11 to 19 kcal/mol and carbene formation is exothermic by over 100 kcal/mol, there is ample energy to accomplish the interconversions. It is clear that carbenes **1**−**3** generated in these reactions have the thermodynamic properties predicted by the calculations.

However, the reactivity observed for carbene **1** generated in these C-atom reactions does not completely correspond to that predicted by the calculations. There are two interesting points of disagreement. First, singlet **1** is expected to undergo intramolecular C−H insertion to give dihydrobenzofuran **8** more readily than it ring-expands to either **12** or **13**. As **6** and **11** can be generated from (reversible) ring expansion prior to trapping processes, one can estimate the ratio of ring expansion to

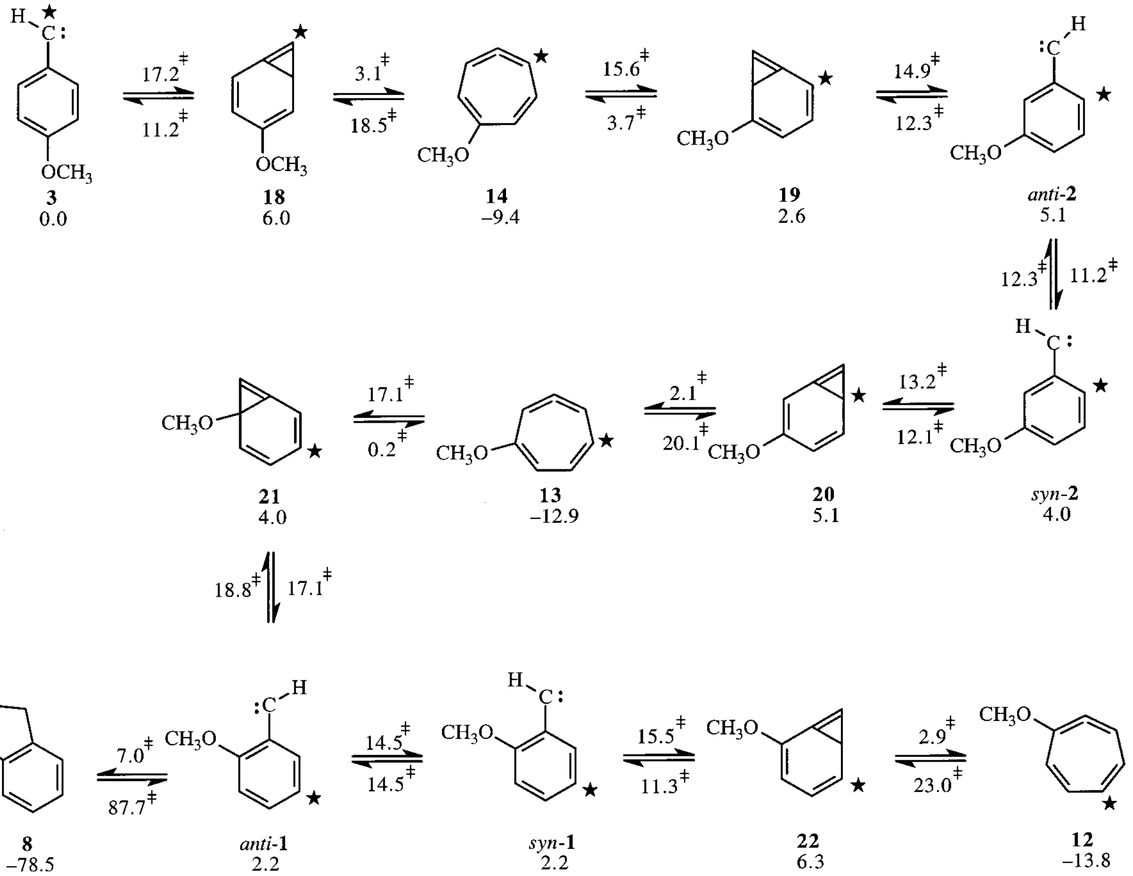


Figure 2. Relative energy (kcal/mol) of the stationary points involved in the reversible ring expansion of methoxyphenylcarbene calculated at the B3LYP/6-311+G**//B3LYP/6-31G* level of theory. Activation barriers are given relative to the minimum that precedes them in the figure. The lowest energy methoxy conformer of each species is used in the energetic evaluation.

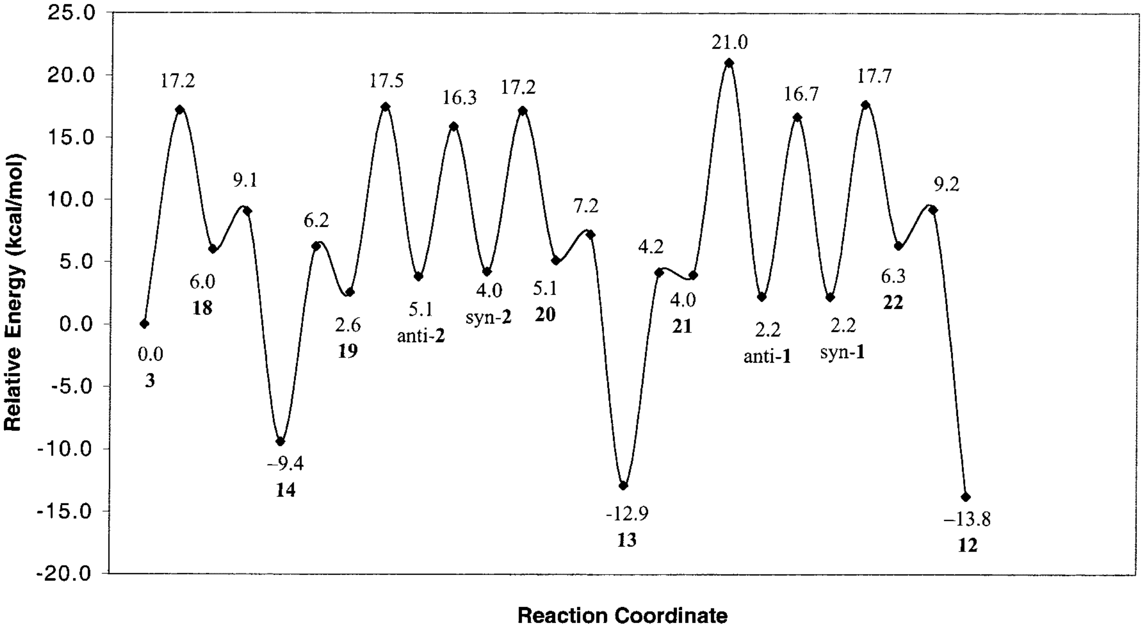


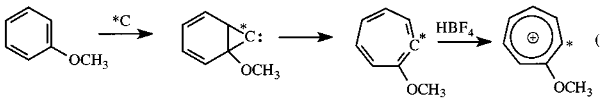
Figure 3. Graphical view of the potential energy surface presented in Figure 2.

intramolecular C−H insertion when carbene **1** is generated by the deoxygenation of **15**. Based on this approach, when **1** is generated from **15**, the ratio of ring expansion to intramolecular C−H insertion is 5.5:1 (as assessed by the ratio of the combined yield of **6** and **11** relative to that of **8**, Table 1). Second, if **1** does ring-expand, it is calculated to cross a lower barrier if it generates **12** rather than **13**. However, this prediction is inconsistent with the label distribution from the reaction of ^{13}C-enriched carbon vapor with **4**, followed by trapping with HBF_4. As shown in Figure 1, C−H insertion by ^{13}C on **4b** generates **1** with the label on the carbene carbon. Subsequent ring expansion to **12** ($\Delta H^{\ddagger} = 15.4$ kcal/mol) and trapping with HBF_4

places the label on C_3 of **11**, while ring expansion to **13** ($\Delta H^{\ddagger}$ = 18.8 kcal/mol) and trapping gives **11**-2-^{13}C. However, the observed ratio of **11**-2-^{13}C to **11**-3-^{13}C is 5:1. Figure 1 demonstrates that **2** from C−H insertion by ^{13}C can ring-expand and be trapped as **11**-3-^{13}C or **11**-4-^{13}C with the formation of **11**-4-^{13}C being the lower energy pathway. Carbene **3** from ^{13}C insertion can only give **11**-4-^{13}C. Thus, an excess of label on C_4 of **11** is consistent with the calculations, while more label at C_2 than at C_3 of **11** is not.

We feel that the difference between the reactivity observed for carbene **1** and that calculated can be attributed to the excess energy imparted to the carbene in its formation. As mentioned earlier, we have presented evidence that the large exothermicity of carbene formation in C-atom reactions can be channeled into the formation of electronically excited singlet carbenes.[10,11] In the present case, we expect that the $^1A_2$ configurations of carbenes **1**−**3** will be energetically accessible.[27] These open-shell singlet phenylcarbenes resemble singlet phenylnitrene,[28] which is known to ring-expand much faster in solution than phenylcarbene.[21d,28] Indeed, Gritsan and co-workers recently showed that fluoro-substituted phenylnitrene undergoes reversible ring expansion.[29] If the phenylnitrene analogy holds for open-shell singlet **1**, ring expansion of *anti*-**1** may be faster than intramolecular C−H insertion to give **8**. We note that it is *anti*-**1** that is calculated to ring-expand to ultimately give the observed **11**-2-^{13}C. If the anti conformer of carbene **1** is formed preferentially in the C-atom reactions, perhaps for steric reasons, and ring expansion is rapid, then the experimental label distribution in **11** seems reasonable.

There are, however, at least two possible alternative explanations for the observed label distribution in **11**, both of which we have explored and discounted. If C atom reacts with **4** by addition to the π bond between C_1 and C_2 and this addition is more favorable than the C_2−C_3 addition, it is possible to obtain **11** with the observed label distribution (eq 8).

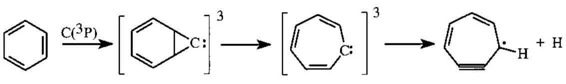


(8)

4 **12**-2-^{13}C **11**

However, there is considerable evidence that singlet C atoms react with benzene rings by C−H insertion rather than by π bond addition. We have used double-labeling experiments to determine that arc-generated C reacts with benzene by C−H insertion.[14] Analysis of the label distribution in products and isotope effects in the reaction of C with *tert*-butylbenzene leads to the same conclusion.[14] The observed label distribution in the reaction of nucleogenic carbon atoms with toluene is also consistent with initial insertion into aromatic C−H bonds rather than π bond addition.[20] Since we see no reason the reaction of carbon with **4** should be different from the above examples, we feel that the present reaction proceeds by C−H insertion to give **1**−**3** as primary products, and it is the excess energy in these carbenes that is responsible for the unusual reactivity.

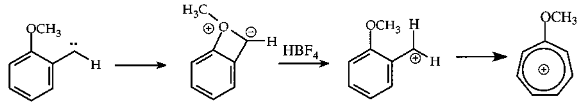
It should be pointed out that the reaction of C(^{3}P) with benzene in a gas-phase molecular beam study is postulated to proceed via a π bond addition as shown in eq 9.[30]



(9)

However, this is a gas-phase reaction of C(^{3}P) which has little analogy to the present experiments. In our experimental investigations of the cocondensation of arc-generated C atoms with **4** at 77 K, we find no evidence for the reaction of C(^{3}P). For instance, addition of oxygen, an efficient scavenger of C(^{3}P), does not affect product yields. We do not think that the lack of products from triplet carbon reflects the absence of this species, which is the ground state of atomic carbon, in our experiment. Instead, we feel that the reaction conditions (condensed phase, 77 K) are not conducive to the reaction of C(^{3}P) with our substrates. Rather, reaction of triplet carbon with itself leads to the copious amount of amorphous carbon we see in these reactions.

Another possible explanation for the preferential ring opening and observed label distribution as well as the lower than expected yield of **8** in the reaction of **1** relies on the formation of a zwitterionic ylide structure, as illustrated below.



(10)

1 **11**

This structure is analogous to the ylide formed in the rearrangement of carbene−ethylene sulfide complexes found by Platz and co-workers.[31] If the zwitterion is adequately stable to persist in the matrix until the addition of HBF$_4$, ring-opening may, in fact, take place from the *o*-methoxybenzyl carbocation directly to the tropylium ion **11**. Calculations were carried out at the B3LYP/6-31G* level of theory to characterize the zwitterion. When the bond distance from the methoxy oxygen to the carbene carbon is fixed and all of the other parameters are completely optimized, the structure has an energy that is ∼30 kcal/mol higher in energy than the *o*-carbene. In fact, when this restraint is released, the structure optimized to the ring-opened *o*-carbene. On the basis of these findings, we have also ruled out the mechanism illustrated in eq 10 and doubt the possibility of the zwitterion as an intermediate in this reaction.

Conclusions

Carbenes can be readily generated in C-atom reactions, but these carbenes have excess energy that can be channeled into unusual reactivity. Although there are certainly examples of carbenes generated by these methods that exhibit “normal” carbene reactivity, it is clear that each case must be examined

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(27) Both experimental (Ref 10 and Herzberg, G.; John, J. W. C. *Proc. R. Soc. London, Ser. A* **1966**, *295*, 107) and theoretical[11] studies place this separation at ∼35 kcal/mol for species as varied as methylene and cyclopentylidene. We believe that there is no reason that the species under consideration here should greatly deviate from this value.

(28) For leading references, see: Borden, W. T.; Gritsan, N. P.; Hadad, C. M.; Karney, W. L.; Kemnitz, C. R.; Platz, M. S. *Acc. Chem. Res.* **2000**, *33*, 765.

(29) Gritsan, N. P.; Gudmundsdottir, A. D.; Tigelaar, D.; Zhu, Z.; Karney, W. L.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 1951.

(30) (a) Kaiser, R. I.; Hahndorf, I.; Huang, L. C. L.; Lee, Y. T.; Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F., III; Schreiner, P. R. *J. Chem. Phys.* **1999**, *110*, 6091. (b) Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F., III; Schreiner, P. R.; Kaiser, R. I.; Lee, Y. T. *J. Chem. Phys.* **2000**, *113*, 4520. (c) Lee, T. N.; Lee, H. Y.; Mebel, A. M.; Kaiser, R. I. *J. Phys. Chem. A* **2001**, *105*, 1847. (d) Ngugen, T. L.; Mebel, A. M.; Kaiser, R. I. *J. Phys. Chem. A* **2001**, *105*, 3284.

(31) Tae, E. L.; Zhu, Z.; Platz, M. S. *Tetrahedron Lett.* **1999**, *40*, 4921.

carefully. Traditionally, such examinations have involved comparing the reactivity of carbenes from a number of different precursors. While this approach is certainly valuable, it suffers from the fact that it is difficult to determine which reactions are those of the "true" carbene. Instead, the approach that we have taken in the present study is to assume that "true" carbene reactivity can be calculated and used as a benchmark.

In the present study, we have observed the reversible ring expansion of methoxyphenylcarbene, analogous to the well-known phenylcarbene process. This ring expansion is observed when the carbene is generated either by direct carbon atom reaction with anisole or by deoxygenation of methoxybenzaldehydes **15**−**17** with carbon atom. Formation of methoxytropylium ion via reaction with HBF_4 as well as the appearance of isomeric methoxytoluenes **5**−**7** is taken as evidence of this reversible ring expansion.

DFT results agree well with the observed product distributions from reaction of carbenes **2** and **3**. However, carbene **1**, the ortho isomer, undergoes a much more facile ring expansion than predicted by calculations. Computational results predict that ring expansion, with a barrier of 17.1 kcal/mol, would not compete with the formation of dihydrobenzofuran **8**, which has an activation barrier of 7.0 kcal/mol. However, when *o*-methoxybenzaldehyde (**15**) is deoxygenated, ring expansion is favored 5.5:1 over formation of **8**. The availability of the open-shell configuration for these arylcarbenes complicates the direct interpretation of the experimental results vis à vis the computational results. We have invoked an explanation here based upon an analogy to the favored ring-expansion process in electronically similar singlet phenylnitrene.

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Supporting Information Available: Cartesian coordinates and frequencies for all compounds discussed and single-point energy computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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