# An Unusual Isotope Effect in the Reactions of the Naphthylcarbenes

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Atomic carbon reacts with benzene and substituted benzenes on the singlet energy surface by an initial C−H insertion to generate a phenylcarbene which can either be trapped by an intramolecular reaction with a substitutent or ring expand to a cycloheptatetraene which can subsequently be trapped.[1−4] We have now used this method to generate the 1- and 2-naphthylcarbenes, **1** and **2**, and have found a remarkable isotope effect upon their reactivity.[5]

Co-condensation of arc-generated carbon with naphthalene **3** at 77 K generates cyclobuta[*de*]naphthalene, **4**, the 1- and 2-methylnaphthalenes, **5** and **6**, along with compounds whose molecular weight indicates that they are products of the reaction of **1** and **2** with **3**, and other uncharacterized products of the reactions of C$_2$ and C$_3$ with **3**. Carbenes **1** and **2** have been well
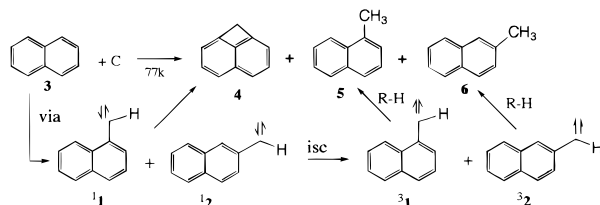


characterized in low-temperature matrixes,[6] in solution,[7] in the gas phase,[8] and computationally.[9] Both **1** and **2** rearrange to **4** at elevated temperatures,[8] and it is clear that the carbenes interconvert under these conditions. Calculations indicate that **4** is the thermodynamic sink and is accessible by rearrangement of **1** ($E_a$ = 23.8 kcal/mol) and from **2** via **1** ($E_a$ = 24 kcal/mol).[9] It thus appears that **4** is formed in our system from chemically activated singlet **1** which is generated in a reaction exothermic by roughly 117 kcal/mol.[10] Possible routes to the methylnaphthalenes include H abstraction by triplet **1** and **2** and/or the

addition of CH$_2$ (from consecutive H abstractions by C) to **3**. That the formation of **4** requires thermal activation is indicated by the fact that raising the temperature of the surface upon which C + **3** is condensed increases the ratio of **4**:(**5** + **6**).

When **1** and **2** were generated independently by the C atom deoxygenation of the 1- and 2-naphthaldehydes, **7** and **8**,[12] **4** was formed in both reactions (Table 1), and we conclude that the exothermicity of the deoxygenation ($\Delta H$ = −112 kcal/mol)[10] brings about the interconversion of **1** and **2**.[12]
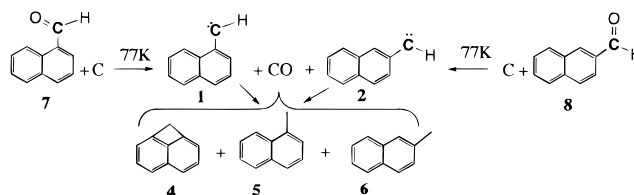


Addition of HBF$_4$ to the C + **3** low-temperature matrix does not trap a benzocycloheptatetraene[13] as benzotropylium ion, and addition of styrene does not trap the strained double bond in a benzobicyclo[4.1.0]heptatriene.[6a] We thus conclude that singlets **1** and **2** either lose their excess energy and react intermolecularly or find their way to the thermodynamic sink, **4**.

The reaction of C with naphthalene-*d$_8$* reveals a dramatic new dimension of reactivity in the naphthylcarbenes produced. As illustrated in Table 1, substitution of **3**-*d$_8$* for **3**-*d$_0$* increases the **4**:(**5** + **6**) ratio by a factor of 26 at 77 K. Moreover, co-condensation of C with a 1:1 mixture of **3**-*d$_0$* and **3**-*d$_8$* generates **4**-*d$_0$* and **4**-*d$_8$* in a 0.12 ratio.

These results appear to indicate an impossibly large inverse deuterium isotope effect on the formation of **4** in this system. Since both the formation of **1** and its rearrangement to **4** involve breaking a C−H bond in nonlinear transition states, modest normal primary isotope effects are expected.[14,15] However, a normal isotope effect upon the rate of intersystem crossing (ISC) in **1** would explain these results. In this scenario, $^1$**1**-*d$_8$* decays to the triplet much slower that $^1$**1**-*d$_0$*, and more **4**-*d$_8$* is generated in the reaction of C with **3**-*d$_8$* than in the reaction of C with **3**-*d$_0$*.

A large $k_H/k_D$ on the rate of ISC predicts more triplet products from **1**-*d$_0$* and **2**-*d$_0$* than from **1**-*d$_8$* and **2**-*d$_8$*. If we assume that **5** and **6** are triplet products, this is certainly the case (Table 1). However, as indicated above, **5** and **6** can also result from the addition of methylene to **3**, and more definitive evidence for triplet products of carbenes **1** and **2** is needed. To further assess the role of triplets in this reaction, we have reacted C with **3**-*d$_0$* and **3**-*d$_8$* in the presence of *E*- and *Z*-2-butene and examined the stereochemistry of the carbene adducts as a function of deuterium content.[17] The results of these experiments, shown in eq 1 for *Z*-2-butene, are quite striking, with 4−18% of the trapped adducts (**10** and **12**) formed with loss of stereochemistry in the case of

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(2) Gaspar, P. P.; Berowitz, D. M.; Strongin, D. R.; Svoboda, D. L.; Tuchler, M. B.; Ferrieri, R. A.Wolf, A. P. *J. Phys. Chem.* **1986**, *90*, 4691.

(3) For a report of the reaction of triplet carbon with benzene in crossed beams experiment, see: Kaiser, R. I.; Hahndorf, I.; Haung, 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.

(4) For reviews of the chemistry of atomic carbon, see: (a) Skell, P. S.; Havel, J. J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, *6*, 97. (b) MacKay, C. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 1−42. (c) Shevlin, P. B. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. I, pp 1−36.

(5) The experimental setup is described in ref 1. Carbon atoms and substrate were co-condensed at 77 K, and products were anaylzed by GC, GC/MS, and NMR.

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(10) This value has been estimated from the heats of formation of C ($^1$D), the organic precursor, and phenylcarbene.[11]

(11) Poutsma, J. C.; Nash, J. J.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 4686.

(12) Deoxygenation of aryl aldehydes is known to generate chemically activated carbenes: Rahman, M.; Shevlin, P. B. *Tetrahedron Lett.* **1985**, *26*, 2959.

(13) Coburn, T. T.; Jones, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5218.

(14) A $k_H/k_D$ = 1.77 has been observed for insertion of carbon into the aromatic C−H bond of *tert*-butylbenzene.[1] A $k_H/k_D$ > 1 for the rearrangement of **1** to **4** was calculated using the method of Bigeleisen and Mayer: Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, 15, 261. The calculations used the program QUIVER (Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989).

(15) A reviewer has made the point that the observed isotope effects could arise from a normal $k_H/k_D$ on the decomposition of **4**. While this reaction has not been studied, byproducts observed when **4** is generated by FVP indicate that the rate-determining step would be cleavage of a C−C bond in the four-membered ring.[16] The $k_H/k_D$ for this step would be small.

(16) Engler, T. A.; Shechter, H. *J. Org. Chem.* **1999**, *64*, 4247 and references cited.

**Table 1.** Relative Yields of Products in the C Atom Generation of Carbenes **1** and **2**

| | | relative yields of products | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| reactants | $T$ (K) | **4** | **5** | **6** | **4/(5+6)** | **9** | **10** | **11** | **12** |
| C + **3** | 77 | 1 | 4.9 | 6.4 | 0.09 | | | | |
| C + **3** | 158 | 1 | 0.67 | 1.2 | 0.55 | | | | |
| C + **3** | 195 | 1 | 0.62 | 0.98 | 0.63 | | | | |
| C + **3** | 273 | 1 | 0.37 | 0.38 | 1.33 | | | | |
| C + **7** | 77 | 1 | 0.145 | 0.035 | 5.55 | | | | |
| C + **8** | 77 | 1 | 0.091 | 0.132 | 4.48 | | | | |
| C + **3**-$d_8$ | 77 | 1 | 0.15 | 0.29 | 2.3 | | | | |
| C + 1:1 **3**-$d_0$:**3**-$d_8$ | 77 | 1 ($d_0$) | 4.1 ($d_0$) | 6.9 ($d_0$) | 0.09 ($d_0$) | | | | |
| | | 1 ($d_8$) | 0.44 ($d_8$) | 0.64 ($d_8$) | 0.92 ($d_8$) | | | | |
| | | $d_0/d_8 = 0.12$ | $d_0/d_8 = 1.1$ | $d_0/d_8 = 1.2$ | | | | | |
| C + 1:1 **3**-$d_0$:**3**-$d_8$ | 195 | $d_0/d_8 = 0.36$ | | | | | | | |
| C + 1:1 **3**-$d_0$:**3**-$d_8$ | 273 | $d_0/d_8 = 0.63$ | | | | | | | |
| C + **3** + Z-2-butene | 77 | 1 | 0.3 | 0.73 | 0.98 | 0.19 | 0.05 | 0.70 | 0.04 |
| C + **3**-$d_8$ + Z-2-butene | 77 | 1 | 0.19 | 0.37 | 1.78 | 0.21 | 0 | 0.29 | 0 |
| C + **3** + E-2-butene | 77 | 1 | 0.64 | 0.84 | 0.68 | 0.08 | 0.34 | 0.07 | 1.1 |
| C + **3**-$d_8$ + E-2-butene | 77 | 1 | 0.18 | 0.3 | 2.08 | 0 | 0.20 | 0 | 0.73 |
| C + 1:1 **3**-$d_0$:**3**-$d_8$ + Z-2-butene | 77 | 1 ($d_0$) | 0.4 ($d_0$) | 0.19 ($d_0$) | 1.68 ($d_0$) | 0.24 ($d_0$) | 0.05 ($d_0$) | 0.75 ($d_0$) | 0.05 ($d_0$) |
| | | 1 ($d_8$) | 0.18 ($d_8$) | 0.07 ($d_8$) | 4.0 ($d_8$) | 0.11 ($d_8$) | 0 ($d_8$) | 0.36 ($d_8$) | 0 ($d_8$) |
| | | $d_0/d_8 = 0.57$ | $d_0/d_8 = 1.2$ | $d_0/d_8 = 1.8$ | | $d_0/d_8 = 1.2$ | | $d_0/d_8 = 1.2$ | |

**3**-$d_0$ while the deuterated counterparts of these compounds cannot be detected in the reaction of C with **3**-$d_8$ and Z-2-butene. These



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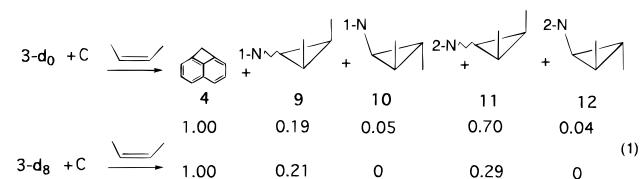
effects are mirrored in the reactions of C with **3** in the presence of E-2-butene and in the reactions of 1:1 **3**-$d_0$:**3**-$d_8$ with C and Z-2-butene (Table 1). Thus, triplet trapping products are formed from the protiated but not the deuterated carbenes, a finding consistent with $k_H/k_D > 1$ for ISC. In general, we observe that **1**-$d_8$ and **2**-$d_8$ always give more **4** than do **1**-$d_0$ and **2**-$d_0$, which give more intermolecular products.[18]

When the reaction of C with a 1:1 mixture of **3**-$d_0$ + **3**-$d_8$ is carried out in the presence of oxygen,[19] triplet **1** and **2** are trapped as naphthaldehydes **7** and **8** (eq 2). Although oxygen is a more



(2)
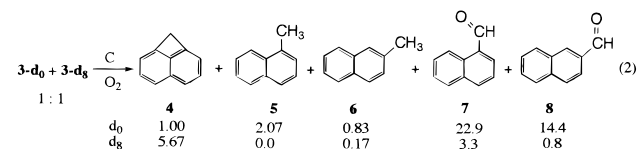
effective triplet trap that 2-butene, the results for the two systems

(17) A layer of 2-butene was placed in the reactor at 77 K, C and **3** were co-condensed, and the process was repeated. Compounds **9**−**12** were independently synthesized by the photolysis of the corresponding diazo compounds in the presence of E- and Z-2-butene (giving stereospecific addition) and characterized by NMR and GC/MS. *syn*- and *anti*-**9** and -**11** were not separated for the NMR spectra but were separable by GC. When **9**−**12** were generated in C atom reactions, all $d_0$ compounds were separable from $d_8$ compounds in the GC/MS.

(18) Ratios of **4**:(**5** + **6**) always increase when an organic matrix such as 2-butene or THF is added to the reactor. We attribute this effect to stabilization of the singlet carbene by the matrix. Since this effect also ameliorates the isotope effects (C + **3**-$d_0$ on THF yields **4**:(**5** + **6**) = 1.44, while C + **3**-$d_8$ on THF yields **4**:(**5** + **6**) = 3.70), isotope effects in the presence and absence of 2-butene cannot be directly compared.

(19) Reactions in the presence of O$_2$ were carried out with a constant pressure of 5.6 Torr O$_2$. Increasing this pressure increases the ratio of (**7** + **8**):(**5** + **6**).

are similar in that far more triplet-$d_0$ products than triplet-$d_8$ products are formed. Since oxygen is an extremely effective scavanger of C($^3$P),[4] this experiment also rules out C($^3$P) as a source of triplet **1** and **2**.

Isotope effects upon radiationless transitions are well documented in photochemical systems.[20−23] The usual explanation given for normal isotope effects upon nonradiative decay is the fact that the higher energy C−H vibrations require less quanta to match an electronic gap with vibrational energy than do C−D vibrations. Hence, the Franck−Condon overlaps and thus the probability of surface crossings are greater in the protiated compounds.[20] However, as the gap between states decreases, the isotope effects can shift from normal to inverse due to a higher density of levels in the accepting deuterated state.[24,25] Since the S−T splittings in **1** and **2** are only about 5 kcal/mol,[9] we may have expected an inverse isotope effect on the S−T transitions. However, our normal isotope effects are indicative of a larger energy gap, and we feel that they result from the generation of the singlet state of **1** and **2** with excess energy and it is the isotope effect upon the degradation of the energetic carbene to the triplet state that we are observing. These arguments predict that similar isotope effects will not be observed when **1**-$d_8$ and **2**-$d_8$ are generated from conventional less energetic carbene precursors. We are currently examining this possibility and searching for this phenomenon in other energetic deuterated carbenes.

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