

Mode of Attack of Atomic Carbon on Benzene Rings

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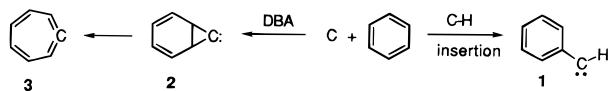
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Abstract: Reaction of arc generated carbon atoms with *tert*-butylbenzene, **4**, gives 3-methyl-3-phenyl-1-butene, **5**, and 1,1-dimethylindane, **6**. Labeling studies and isotope effects demonstrate that **5** results from an insertion into a methyl C–H bond followed by 1,2 hydrogen shift while **6** arises from initial ortho C–H insertion followed by intramolecular insertion into a methyl C–H bond. When fluoroboric acid is added to the 77 K matrix of **4** + C, *tert*-butyltropylium fluoroborate, **18**, is formed. Labeling studies indicate that **18** results from initial insertion of C into meta and para C–H bonds of **4** followed by ring expansion to cycloheptatetraenes which are subsequently protonated. The reaction of C with benzene gives similar results, indicating that initial C–H insertion is the preferred mode of attack of atomic carbon on benzene rings.

Introduction

Although the reaction of atomic carbon with benzene and its derivatives has been the subject of many investigations,¹ the site of initial attack by carbon remains an unanswered question. It is reasonable to assume that this reaction, which provides an entry to the C₇H₆ energy surface, proceeds either by a C–H insertion to generate phenylcarbene, **1**, or by double bond addition (DBA) to give an initial bicycloheptadienylidene, **2**, which may be expected to ring open to cycloheptatetraene, **3**. Although investigations of the reaction of C with benzene have



invariably led to products ascribable to the intermediacy of **1** and **3**,¹ the situation is complicated by the fact that these species are interconvertible through the extensively investigated phenylcarbene rearrangement.^{2,3} It is clear that isotopic labeling studies are required to solve this problem and that a fruitful approach will involve the use of a molecule with an available intramolecular trap.

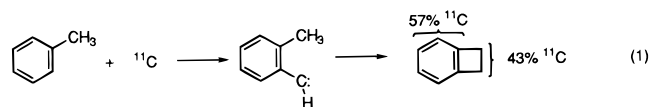
Such a study is reported in the elegant work of Gaspar, Berowitz, Strongin, Svoboda, Tuchler, Ferrieri, and Wolf,⁴ who

(1) (a) Wolf, A. P.; Redvanly, C. S.; Anderson, R. C. *Nature* **1955**, 176, 831. (b) Schrodt, A. G.; Libby, W. F. *J. Am. Chem. Soc.* **1956**, 78, 1267. (c) Suryanarayana, B.; Wolf, A. P. *J. Phys. Chem.* **1958**, 62, 1369. (d) Sprung, J. L.; Winstein, S.; Libby, W. F. *J. Am. Chem. Soc.* **1965**, 87, 1812. (e) Rose, T.; MacKay, C.; Wolfgang, R. *J. Am. Chem. Soc.* **1967**, 89, 1529. (f) Williams, R. L.; Voigt, A. F. *J. Phys. Chem.* **1969**, 73, 2538. (g) Lemmon, R. M. *Acc. Chem. Res.* **1973**, 6, 65 and references therein. (h) Biesiada, K. A.; Koch, C. T.; Shevlin, P. B. *J. Am. Chem. Soc.* **1980**, 102, 2098.

(2) For reviews of experimental work with many references see: (a) Jones, W. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1. (b) Wentrup, C. In *Methoden der Organischen Chemie (Houben-Weyl)*; Regitz, M., Ed.; G. Thieme: Stuttgart, 1989; Vol. E19b, pp 824–1021. (c) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M. *Tetrahedron* **1985**, 41, 1479–1507. (d) Platz, M. S. *Acc. Chem. Res.* **1995**, 28, 487–492.

(3) Recent theoretical work includes: (a) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon R. J. *J. Am. Chem. Soc.* **1996**, 118, 1535. (b) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, 61, 7022. (c) Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F., III *J. Org. Chem.* **1996**, 61, 7030. (d) Cramer, C. J.; Dulles, F. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1994**, 116, 9787.

studied the reaction of nucleogenic ¹³C atoms with toluene. In this case the methyl group traps an initially formed *o*-tolylcarbene as benzocyclobutene. A partial degradation of the benzocyclobutene and an examination of the label distribution indicated that 43% of the benzocyclobutene arose from *o*-tolylcarbene formed by an initial C–H insertion (eq 1). The remainder of the label in the benzocyclobutene was in the ring, indicating the initial formation of the *m*- and *p*-tolylcarbenes.



We have recently reported several investigations in which we have used ¹³C enriched arc generated carbon vapor to elucidate the mechanisms of reaction of atomic and molecular carbon.^{5,6} We now report a study of the reaction of ¹³C atoms with benzene and *tert*-butylbenzene in which we demonstrate that products result from a phenylcarbene formed by an initial C–H insertion.

Results and Discussion

Reaction of Atomic Carbon with *tert*-Butylbenzene. Since the reaction of arc generated C with toluene gives an extremely complex product mixture,⁷ our initial studies have focused on the reaction of C with *tert*-butylbenzene, **4**, which gives 3-methyl-3-phenyl-1-butene, **5**, and 1,1-dimethylindane, **6**, as the only major products in a 2:1 ratio. When ¹³C enriched C

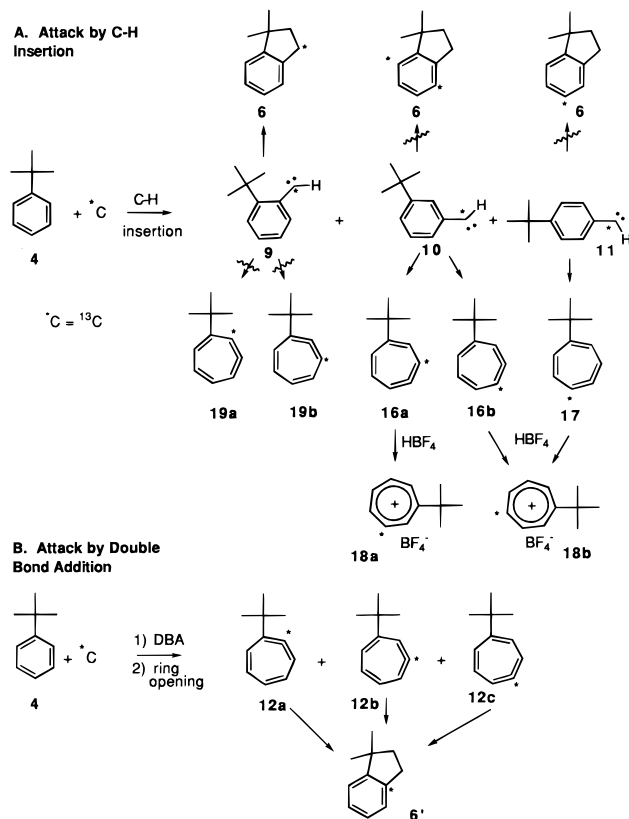
(4) Gaspar, P. P.; Berowitz, D. M.; Strongin, D. R.; Svoboda, D. L.; Tuchler, M. B.; Ferrieri, R. A.; Wolf, A. P. *J. Phys. Chem.* **1986**, 90, 4691.

(5) (a) Emanuel, C. J.; Shevlin P. B. *J. Am. Chem. Soc.* **1994**, 116, 5991. (b) Pan, W.; Shevlin, P. B. *J. Am. Chem. Soc.* **1996**, 118, 10004. (c) Pan, W.; Balci, M.; Shevlin, P. B. *J. Am. Chem. Soc.* **1997**, 119, 5035. (d) Pan, W.; Shevlin, P. B. *J. Am. Chem. Soc.* **1997**, 119, 5091.

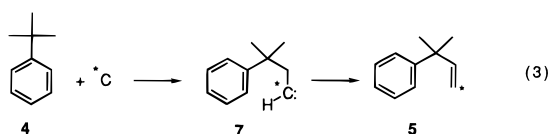
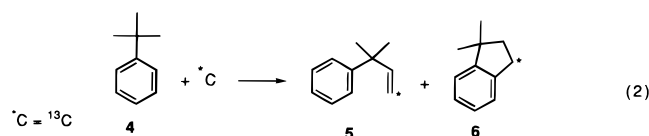
(6) For reviews of the chemistry of atomic carbon see: (a) Skell, P. S.; Havel J. J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, 6, 97. (b) MacKay, C. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 1–42. (c) Shevlin, P. B. in “Reactive Intermediates”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

(7) Although this reaction does give benzocyclobutene, the complexity of the reaction mixture is due in part to secondary reactions of the styrene produced.

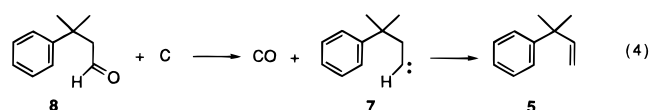
Scheme 1



vapor was used, an examination of the ^{13}C NMR spectra of the products indicated that **5** was labeled in the 1-position and **6** in the 3-position (eq 2). It is likely that **5** results from an initial



insertion into a methyl C–H bond to give carbene **7** followed by a 1,2-hydrogen shift (eq 3). The possibility that **6** results from an intramolecular insertion of **7** into an ortho C–H bond is ruled out by generating **7** by the C atom deoxygenation of aldehyde **8** and observing that **5** is the only product (eq 4).⁸

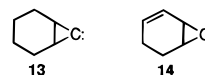


Scheme 1, which shows the anticipated label distribution in **6** resulting from all possible C–H insertions and DBAs of ^{13}C with **4**, indicates that the most reasonable path to **6**- $3\text{-}^{13}\text{C}$ is ortho C–H insertion to give *o*-*tert*-butylphenylcarbene, **9**, which undergoes intramolecular insertion into a methyl C–H bond.

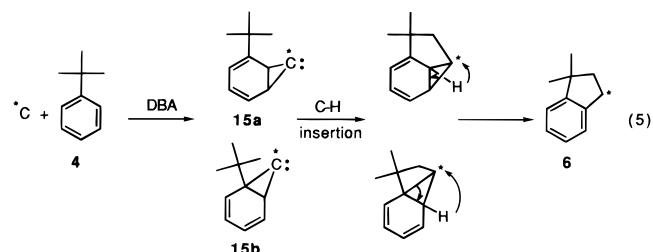
(8) Carbon atom deoxygenation of carbonyl compounds is a well documented route to carbenes. See: Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 3685 and references therein.

The production of **6** by initial insertion into a meta or para C–H bond to give **10** or **11** followed by phenylcarbene rearrangement to **9** would place the label on the aromatic methylene carbons of **6**. An initial DBA followed by ring expansion to **12a–c** and phenylcarbene rearrangement would have resulted in **6'**, which is not observed.

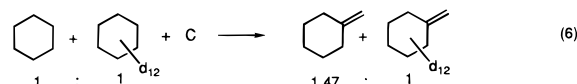
However, analogy with bicycloheptanylidene, **13**, which reacts by intramolecular C–H insertion,⁹ and bicycloheptenylylidene, **14**, which undergoes a Skattebøl rearrangement,¹⁰ indicates that an initially formed *tert*-butylbicycloheptadi-



enylylidene, **15a** or **15b**, could undergo intramolecular C–H insertion to generate **6** rather than ring expand (eq 5).



If this is the case, initial reaction by carbon would not involve the breaking of a C–H bond and little discrimination between attack on a C–H or C–D bond would be expected. Accordingly, we have reacted a mixture of **4** and **4**- d_{14} with carbon and have found that **5** and **6** are formed with observed $k_{\text{H}}/k_{\text{D}}$ values of 1.59 and 1.77, respectively. Although these isotope effects are rather small, they are similar to those observed for carbene C–H insertions^{11,12} and characteristic of nonlinear transition states of the type expected here.¹³ To determine the isotope effect on a C atom reaction which must involve an initial C–H insertion, carbon was reacted with a mixture of cyclohexane and cyclohexane- d_{12} . This reaction led to the formation of methylenecyclohexane and methylenecyclohexane- d_{12} with an observed $k_{\text{H}}/k_{\text{D}} = 1.47$ (eq 6). The observed $k_{\text{H}}/k_{\text{D}}$ when C reacts with a mixture of pyrrole and pyrrole- d_5 , a process known to involve an initial DBA,^{5d} is 1.03.¹⁴



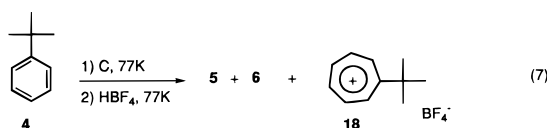
These results indicate that both **5** and **6** are formed with similar primary isotope effects which are indicative of an initial C–H insertion and rule out the formation of **6** by the mechanisms in eq 5. When *tert*-butyl- d_9 -benzene is reacted with C, the ratio of **5**- d_9 to **6**- d_9 is 1.2:1 as compared to 2:1 in the undeuterated case.

Although these experiments lead to the conclusion that **6** is the exclusive result of an initial insertion by carbon into an ortho C–H bond of **4**, it is unreasonable to assume that carbon would be selective in its C–H insertions and we are left to wonder

(9) (a) Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019. (b) Köbrich, G.; Goyert, W. *Tetrahedron* **1968**, *24*, 4327.
 (10) Warner, P.; Chu, I.-S. *J. Org. Chem.* **1984**, *49*, 3666.
 (11) Franzen, V.; Edens, R. *Justus Liebig's Ann. Chem.* **1969**, *729*, 33.
 (12) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; p 240.
 (13) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 785.
 (14) Pan, W. Ph.D. Thesis, Auburn University, December 1997.

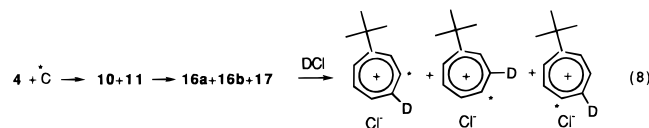
about the fate of the products of insertion into meta and para C–H bonds, **10** and **11**. The labeling distribution in **6** tells us that **10** and **11** do not undergo phenylcarbene rearrangement to **9**. If **10** and **11** lack the energy to undergo any intramolecular reaction, we may expect decay to triplet ground states and subsequent hydrogen abstraction. However, examination of the reaction products does not show any that could be attributed to H abstraction by **10** and **11**.

Recent computational results indicate that the first step of the phenylcarbene rearrangement, ring expansion of **1**, must surmount a barrier of ~ 13 kcal/mol to give **3**.³ However, rearrangement back to **1** (in this case interconverting **9**, **10**, and **11** as shown in Scheme 1) must cross a barrier of ~ 30 kcal/mol, and it may be that initial ring expansion of **10** and **11** leads to cycloheptatetraenes **16a,b** and **17** which, lacking the energy to rearrange further, are polymerized during workup. In support of this assumption, we find that addition of an ethereal solution of HBF₄ to the 77 K reactor bottom results in the formation of *tert*-butyltropylium fluoroborate, **18**, along with **5** and **6** (eq 7). It is likely that **18** results from protonation of an extremely reactive cycloheptatetraene. When the HBF₄ is added to the



reactor after warming to room temperature, no **18** is formed. Addition of HBF₄ to the cold products of the reaction of ¹³C enriched carbon vapor with **4** results in **18a** and **18b** which contain excess ¹³C in the 3 and 4 positions in a 1:2 ratio and no excess ¹³C in the 2 position (Scheme 1). This result indicates that **10** and **11** ring expand to ultimately yield **18** labeled in the 3 and 4 positions while **11** gives only 4-labeled **18**, statistical insertion of C into the ortho and para positions of **4** will yield the observed label distribution in **18**. The fact that the 2 position in **18** is unlabeled and that the 3 and 4 positions are labeled in a 1:2 ratio indicates that **9** does not ring expand to **19a,b**. Instead, **9** is trapped by intramolecular C–H insertion to give **6**.

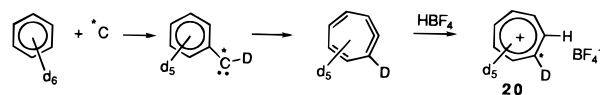
When a double labeling experiment is carried out by adding DCI to the cold matrix of **4** + ¹³C (eq 8), the resultant tropylium salt shows a deuterium signal in the ²H NMR spectrum but no evidence of deuterium attachment to the labeled carbons in the ¹³C spectrum.¹⁵ This result rules out an initial DBA to form



12b and **12c** which would be subsequently deuterated on the labeled carbon.

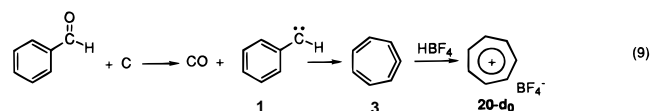
Reaction of C with Benzene. To confirm the generality of this reaction, we have reacted ¹³C atoms with benzene-*d*₆ and added HBF₄ to the cold matrix generating tropylium fluoroborate, **20**. The ¹³C NMR spectrum of **20** shows only a triplet (*J* = 25.5 Hz) due to C–D coupling.

(15) In a typical reaction, the enriched C vapor contains approximately 6% ¹³C. Thus we estimate that the ratio of ¹³CH:¹³CD at C₃ = 4.5 and at C₄ = 6.45. Since the ¹³CD signal is split into a triplet, further decreasing the relative intensities, the triplet for the ¹³CD signal, resulting from the natural abundance of ¹³C in **4**, is not observable.



The results of these experiments indicate that atomic carbon reacts with benzene rings to generate phenylcarbenes by C–H insertion. Since this reaction is exothermic by ~ 115 kcal/mol,¹⁶ there is enough energy in the product to overcome the ~ 13 kcal/mol required for rearrangement to the more stable cycloheptatetraenes.³ However, in the reaction of C with **4**, it appears that the *tert*-butyl substituent on the cycloheptatetraene (**16a**, **16b**, or **17**) lends sufficient degrees of freedom to allow energy dissipation such that the molecule is not able to surmount the ~ 30 kcal/mol barrier for rearrangement back to an isomeric phenylcarbene. We are currently examining the effect of smaller benzene ring substituents on the products of this reaction.¹⁹ The fact that rearrangement of **9** to **19a,b** is not observed indicates that the barrier to intramolecular C–H insertion to give **6** is lower than that for ring expansion to **19a,b**.

To test our postulate that the exothermicity of the carbon atom reaction is sufficient to bring about the ring expansion of **1** to **3**, we have generated **1** by the C atom deoxygenation of benzaldehyde at 77 K. Since this reaction is estimated to be exothermic by ~ 116 kcal/mol, we again expect rearrangement to **3** under the reaction conditions. This expectation is confirmed by adding HBF₄ to the 77 K C + benzene matrix and observing the formation of **20-d**₀ (eq 9).



Summary. The examples presented here along with previous work⁴ demonstrate that carbon atoms react with benzene rings by C–H insertion rather than by DBA. These results are in contrast to the reaction of C atoms with pyrrole in which DBA is the exclusive process^{5a,d} and with thiophene which shows a mixture of C–H insertion, DBA, and attack at sulfur.^{5c} While the reason for the preference for C–H insertion by carbon in its reaction with benzene rings must await a detailed examination of the potential energy surface by sophisticated computational techniques, we note that a thermodynamic preference for the formation of **1** over the highly strained bicycloheptadienylidene, **2**, is expected and it is possible that these thermodynamics are reflected in the relative rates of formation of the two species. These reactions, which provide alternate routes to the C₇H₆ energy surface, may facilitate the elucidation of additional chemistry of the elusive cycloheptatetraene and its derivatives.

Experimental Section

General Information. All ¹H and ¹³C NMR were recorded on Bruker AM 250 or Bruker AM 400 spectrometers. Infrared spectra were obtained with an IR-44 IBM FT-IR. GC analysis were carried out on a Shimadzu GC 14-A instrument with a 30 m × 0.25 mm o.d. DB-5 column. The GC/MS were recorded on a Fisons Trio 2000

(16) A ΔH_f of 103 kcal/mol¹⁷ and a singlet–triplet splitting of 2.3 kcal/mol¹⁸ for **1** were used to determine this value.

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

(18) Admasu, A.; Gudmundsdóttir, A. D.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 3832.

(19) We have reported interconversion of the tolylcarbenes resulting from tolylaldehyde deoxygenation by atomic carbon. Rahman, M.; Shevlin, P. B. *Tetrahedron Lett.* **1985**, *26*, 2959.

quadrupole spectrometer interfaced with a Hewlett-Packard Series II 5890 gas chromatograph equipped with 30 m \times 0.25 mm o.d. DB-5 column. *tert*-Butylbenzene, tropylium hexachlorophosphate, trityl fluoroborate, ethereal fluoroboric acid, and *tert*-butyl chloride were used as received from Aldrich. Benzene-*d*₆, cyclohexane-*d*₁₂, and *tert*-butyl chloride-*d*₉ were used as received from Cambridge Isotopes. 3-Methyl-3-phenyl-1-butene, **5**,²⁰ 1,1-dimethylindane, **6**,²¹ and *tert*-butyltropylium fluoroborate, **18**,²² were prepared by literature methods.

Reaction of Atomic Carbon with *tert*-Butylbenzene. The carbon arc reactor was modeled after that described by Skell, Wescott, Golstein, and Engel.²³ The quantities of carbon given below are calculated from the loss of weight of the graphite. Since most of the carbon is lost in macroscopic pieces, yields based on carbon are not meaningful. Carbon (125 mmol) was vaporized by striking an intermittent arc between two graphite rods attached to water-cooled brass electrodes and condensed on the 77 K walls of the reactor with *tert*-butylbenzene (11.2 mmol) at 5×10^{-5} Torr. When the reaction was over, the reactor bottom was extracted with methylene chloride and the extract filtered and concentrated by rotary evaporation. The resulting products were identified by GC and GC/MS: 3-methyl-3-phenyl-1-butene, **5**, and 1,1-dimethylindane, **6**, were formed in a 2.0:1.0 ratio. The yield of **5** was 3.2×10^{-2} mmol.

Reaction of ¹³C-Enriched Carbon Vapor with *tert*-Butylbenzene. The normal graphite rods which were used in these experiments were altered by drilling a 1/8 in. hole into each individual rod to a depth of 0.75 in. The resulting holes were packed with amorphous ¹³C powder (0.18 g). During this tedious process, small amounts of the powder were added to the hole by a specially made funnel. After each small quantity of powder was added to the hole in the rod, it was packed firmly with a small dowel. This process was repeated until both graphite rods were tightly filled with ¹³C powder. These rods were installed on brass electrodes and the reactor was assembled and evacuated as usual. After the reactor had reached its ultimate vacuum, the two graphite rods were firmly placed head to head (packed hole against packed hole) and the power was turned on. The two rods started to glow red and absorbed gases were evolved. Power was turned off for brief periods to let the rods cool. The heating of the rods to degas the packed amorphous carbon-13 was carried out until no more gas was evolved.

tert-Butylbenzene (11.2 mmol) was condensed on the walls of the reactor bottom at 77 K with ¹³C enriched atomic carbon (65.3 mmol) and the products isolated as above and identified by ¹H and ¹³C NMR, GC, and GC/MS. 3-Methyl-3-phenyl-1-butene, **5**, and 1,1-dimethylindane, **6**, were formed in a 2:1 ratio. A comparison of the intensities of the ¹³C NMR signals of **5** and **6** with those of **5** and **6** from the reaction of unlabeled carbon with **4** (taken under identical NMR conditions) revealed that the signal for C₁ had increased by a factor of 11.0 in **5** and the signal for C₃ in **6** had increased by a factor of 10.0. No other enrichments were observed.

Preparation of *tert*-Butylbenzene-*d*₁₄. Benzene-*d*₆ (0.084 mol) was added to anhydrous aluminum chloride (0.012 mol). The flask was kept at 0 °C with an ice bath and all inlets were protected by drying tubes.

tert-Butyl-*d*₉ chloride (0.02 mol) was added dropwise over 3 h and the mixture was allowed to stir for another hour. D₂O (5 mL) was added to the flask and the mixture allowed to stir for 10 min. The mixture was extracted with ether and dried with magnesium sulfate. The fraction which distilled at 163–166 °C was collected as *tert*-butylbenzene-*d*₁₄ (2.0 g, 68.0%): MS *m/e* (rel intensity) 149 (5), 148 (100), 131 (31), 130 (97), 129 (15), 110 (26), 99 (14), 98 (97), 84 (19), 82 (48), 70 (21), 66 (16), 54 (33), 52 (12), 46 (41), 42 (29).

Reaction of Atomic Carbon with a 1:1 Mixture of *tert*-Butylbenzene-*d*₁₄ and *tert*-Butylbenzene-*d*₀. An equimolar mixture of *tert*-butylbenzene-*d*₀ and -*d*₁₄ (6.6 mmol) was condensed with atomic carbon

(75 mmol) and the products isolated as described above. The products were analyzed by GC and GC/MS. In all cases the *d*₁₄ and *h*₁₄ substrates and products were >95% of the isotopomers as determined by MS and could be separated by GC. 3-Methyl-3-phenyl-1-butene-*d*₀ and -*d*₁₄ were formed in a 1.59:1 ratio. 1,1-Dimethylindane-*d*₀ and -*d*₁₄ were formed in a 1.77:1 ratio. 3-Methyl-3-phenyl-1-butene-*d*₀ and 1,1-dimethylindane-*d*₀ were formed in 2:1 ratios. 3-Methyl-3-phenyl-1-butene-*d*₁₄ and 1,1-dimethylindane-*d*₁₄ were formed in 2.2:1 ratios.

Preparation of *tert*-Butylbenzene-*d*₉. Benzene (0.084 mol), anhydrous aluminum chloride (0.012 mol), and *tert*-butyl-*d*₉ chloride (0.02 mol) were reacted as described above. The fraction which distilled at 164–168 °C was collected as *tert*-butylbenzene-*d*₉ (2.1 g, 73.0%): MS *m/e* (rel intensity) 143 (11), 142 (25), 141 (19), 140 (41), 139 (23), 138 (16), 137 (11), 127 (3), 126 (26), 125 (72), 124 (91), 123 (100), 122 (53), 121 (35) 95 (16), 94 (56), 93 (93), 92 (76), 91 (11), 78 (26), 77 (17), 51 (20), 45 (14), 44 (14), 43 (8), 42 (12), 41 (12), 40 (10), 39 (8).

Reaction of Atomic Carbon with *tert*-Butylbenzene-*d*₉. *tert*-Butylbenzene-*d*₉ (6.5 mmol) was reacted with atomic carbon (91 mmol) and the products isolated as described above. The products were analyzed by GC and GC/MS. 3-Methyl-3-phenyl-1-butene-*d*₉ and 1,1-dimethylindane-*d*₉ were formed in a 1.2:1 ratio and were >95% of the isotopomers.

Reaction of Atomic Carbon with a 1:1 Ratio of Cyclohexane-*d*₁₂ and Cyclohexane-*d*₀. An equimolar mixture of cyclohexane-*d*₀ and -*d*₁₂ (11.9 mmol) was condensed with atomic carbon (134 mmol) and the products isolated as described above. The products were analyzed by GC and GC/MS. The *d*₁₂ and *d*₁₂ substrates and products could be separated by GC. Methylene-cyclohexane-*d*₀ and -*d*₁₂ were formed in a 1.47:1 ratio and were >95% of the isotopomers.

Reaction of Atomic Carbon with *tert*-Butylbenzene followed by the Addition of HBF₄. *tert*-Butylbenzene (6.5 mmol) was reacted with atomic carbon (91 mmol) as described above. Before the reactor was allowed to warm, 1 mL of an ethereal solution of HBF₄ (7.3 mmol) was distilled in. The reactor was allowed to warm to room temperature and extracted with acetonitrile. The extract was filtered, the volatiles evaporated, and the residue taken up in 0.5 mL of D₂O or CD₃CN, and the resultant *tert*-butyltropylium fluoroborate, **18** (the only compound detectable by ¹³C NMR) was analyzed by NMR: ¹H NMR (δ , 400 MHz, CD₃CN) δ 1.58 (s, CMe₃), 9.05 (m, H₃), 9.08 (m, H₄), 9.35 (m, H₂). ¹³C NMR (δ , 100 MHz, CD₃CN) 31.45 (CH₃), 153.99 (C₂), 154.19 (C₄), 154.44 (C₃), 184.14 (C₁). Protons were assigned from the proton–proton correlation spectrum and the carbons from the carbon–proton correlation spectrum.

Reaction of ¹³C-Enriched Carbon Vapor with *tert*-Butylbenzene followed by the Addition of HBF₄. *tert*-Butylbenzene (11.2 mmol) was condensed on the walls of the reactor bottom at 77 K with ¹³C enriched atomic carbon (36.7 mmol) and **18** isolated as above and identified by ¹H and ¹³C NMR. Compound **18** was the only compound detectable by ¹³C NMR. ¹³C enrichments were calculated assuming that no ¹³C was incorporated into the methyl groups of **18**. A comparison of the intensity ratios of the ring carbons to the methyl carbons of **18** with those of **18** from the reaction of unlabeled carbon with **4** (taken under identical NMR conditions) revealed a 36.3% increase at C₃ and a 66.2% increase at C₄ and no increase at C₁ or C₂.

Reaction of ¹³C-Enriched Carbon Vapor with *tert*-Butylbenzene followed by the Addition of DCl. *tert*-Butylbenzene (11.2 mmol) was condensed on the walls of the reactor bottom at 77 K with ¹³C enriched atomic carbon (30.0 mmol), gaseous DCl (0.5 mmol) was added before warming. After warming, an ethereal solution of HBF₄ (7.3 mmol) was added and **18** was isolated as above. The ²H NMR spectrum showed a peak at δ 9.2 and the ¹³C NMR showed only singlets for the ring carbons. A comparison of the intensity ratios of the ring carbons to the methyl carbons of **18** with those of **18** from the reaction of unlabeled carbon with **4** (taken under identical NMR conditions) revealed a 77.6% increase at C₃ and a 168.2% increase at C₄ and no increase at C₁ or C₂.

Reaction of ¹³C-Enriched Carbon Vapor with Benzene-*d*₆ followed by the Addition of HBF₄. The reaction was carried out as

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described above by co-condensing carbon (35.0 mmol) with benzene- d_6 (11.2 mmol) and adding HBF_4 (7.3 mmol). Tropylium fluoroborate- d_6 was isolated by using the methods described above. The ^{13}C NMR spectrum showed a triplet centered at $\delta = 155.36$ ppm with a splitting of 25.5 Hz.

Reaction of Atomic Carbon with Benzaldehyde followed by the Addition of HBF_4 . Benzaldehyde (18.0 mmol) was reacted with atomic carbon (52 mmol) as described above. Before the reactor was allowed to warm, 1 mL of an ethereal solution of HBF_4 (7.3 mmol) was distilled in. The reactor was allowed to warm to room temperature and extracted with acetonitrile. The extract was filtered, the solvent

evaporated, and the residue taken up in CD_3CN , and the resultant tropylium fluoroborate was analyzed by ^1H NMR (δ , 250 MHz, $\text{CD}_3\text{-CN}$): δ 9.2 (s).

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