

Benzocyclohex-1-en-3-yne at High Temperature

Peter J. Lu, Weitao Pan, and Maitland Jones, Jr.*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544

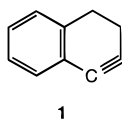
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Abstract: Generation of benzocyclohex-1-en-3-yne in two ways leads to naphthalene and methyleneindene (benzofulvene). Labeling studies favor a multistep mechanism involving an initial electrocyclic ring opening, and carbene–alkene interconversions.

In the phenylcarbene rearrangement (PCR)¹ and the interconversion of phenylnitrene and pyridylcarbene,² an exo-ring methine or nitrogen becomes incorporated into the ring, as a ring vertex takes its place in the exo-ring position (Figure 1). A similar process occurs in carboranylcarbene.³

The graphic device in Figure 2 allows the construction of any of the carbenes available through these rearrangements. In each process a formally sp hybridized group enters the ring (or cage). We wondered if an acetylene could be coaxed into undergoing a related reaction. In such a process, a divalent carbon would be left behind (Figure 3), and it seemed that a suitable molecule could be constructed that would trap both the emerging and residual carbenes. Of course, simple acetylenes are very poor candidates for this reaction, and it seemed prudent to provide some impetus in the form of ring strain. Reactions are known in which acetylenes formally act as dicarbenes,⁴ and of course, the conversion of alkynes into a different kind of carbene, vinylidenes, which was pioneered by Roger Brown and the Australian pyrolysis group,⁵ has found recent spectacular application in L. T. Scott's remarkable synthesis of corannulene.⁶

Such reasoning, together with perhaps more than a modicum ofchutzpah, led to the idea of examining the chemistry of benzocyclohex-1-en-3-yne (**1**) at high temperature. In the end,



we were able to show that our imagined reaction was preempted by another process, but much fascinating chemistry was uncovered and we report it here.

Two routes to **1**, shown below, seemed likely to yield this intermediate (Figure 4). Indeed, related intermediates with one

(1) For a review, see: Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479.

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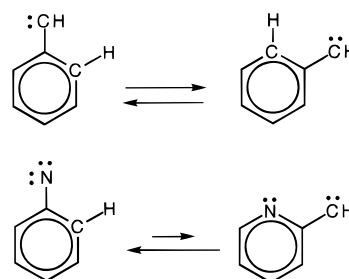


Figure 1.

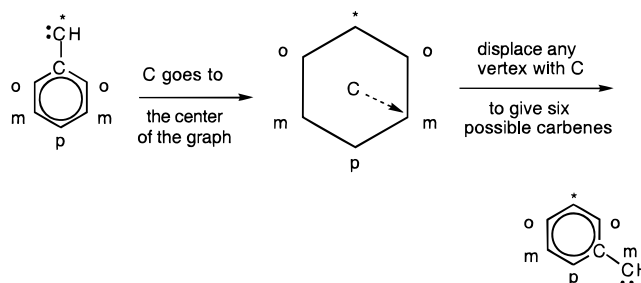


Figure 2. In this version of the graph, an old meta carbon becomes the new divalent center.

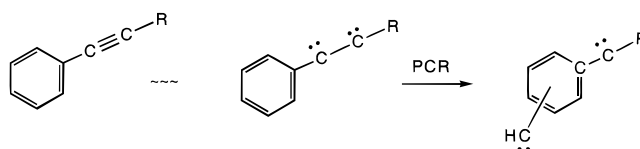


Figure 3.

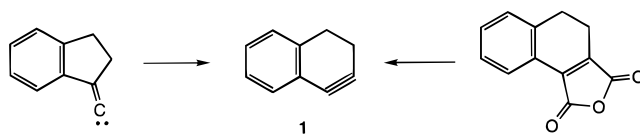


Figure 4.

more double bond have been trapped intramolecularly by the Brown group^{5b} through rearrangement to vinylidenes. The two required precursors, **2** and **3**, were synthesized from an aldol-like condensation of 1-indanone with Meldrum's acid and titanium tetrachloride^{7a} and by the known synthesis of Hershberg and Fieser,^{7b} respectively (Scheme 1). When **2** was dropped onto a hot quartz surface at 640 °C and the products were

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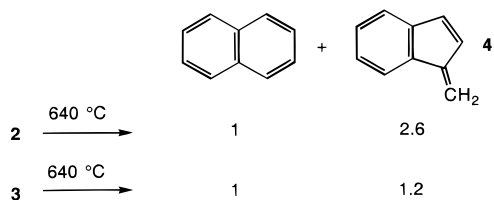
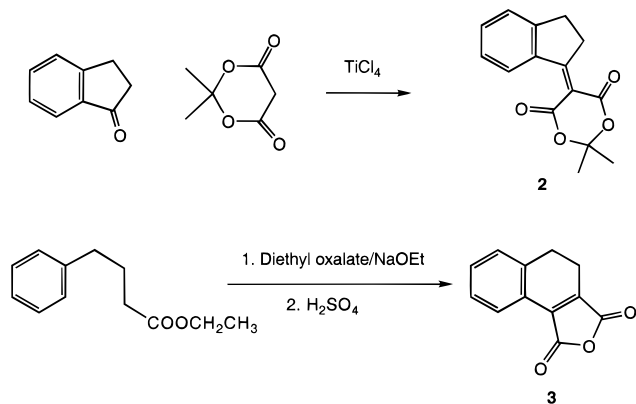
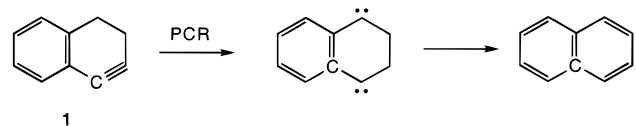


Figure 5.

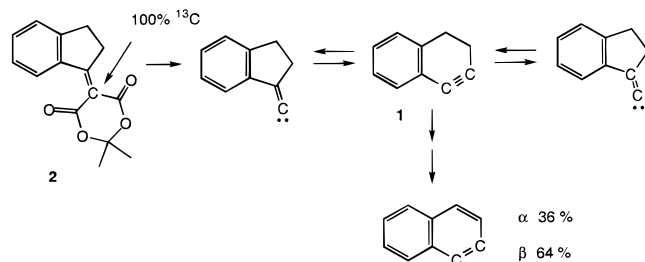
Scheme 1



Scheme 2



Scheme 3



captured in a trap cooled to $-196\text{ }^{\circ}\text{C}$ at 0.005 Torr, naphthalene was formed along with methyleneindene (benzofulvene)⁸ **4** in the ratio 1:2.6. A similar decomposition of **3** at $640\text{ }^{\circ}\text{C}$ led to the same two products in the ratio 1:1.2 (Figure 5).

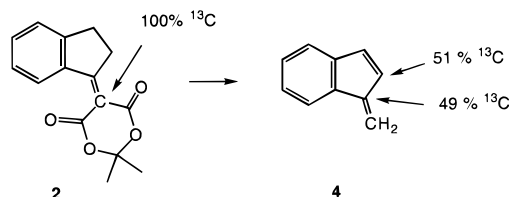
However, a ^{13}C -labeling experiment quickly showed that naphthalene was not formed by our hoped-for mechanism. That route must produce naphthalene with a label in the ring junction (Scheme 2). In fact, decomposition of **2** with 100% ^{13}C in the position shown led to naphthalene with the label distributed between the α and β positions, with no detectable ^{13}C at the ring junction (Scheme 3).⁹ The expected⁵ equilibrium between **1** and the vinylidene would serve to scramble the label, but only the extended phenylcarbene rearrangement could put it at the ring junction.

What was most remarkable, at first, was that there was no label detectable at the methylene position of compound **4**. Clearly, something unusual was going on in the formation of **4** that places one or both of the ring methylenes of **2** in the exoring position of **4**. The apparent transfer of hydrogen from the ring to the divalent carbon cannot be taking place (Scheme 4).

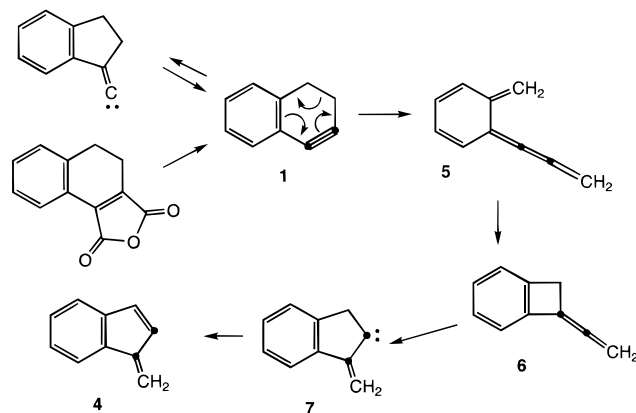
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Scheme 4



Scheme 5



Given all of the evidence for interconversion of vinylidenes and cycloalkynes,⁵ and the similarity of the products from **2** and **3**, it seemed highly likely to us that **1** was formed. Cyclohexyne itself is known to undergo an electrocyclic ring-opening reaction at temperatures above $550\text{ }^{\circ}\text{C}$ to give ethylene and butatriene.¹⁰ Calculations of Johnson and Bradley indicate that cyclohex-1-en-3-yne would also rearrange exothermally to vinyl-1,2,3-butatriene.¹¹ If a related reaction were to occur in **1**, *o*-xylylene **5** would be the product. Surely, given the exothermicity of rearomatization, **5** would rapidly close to **6**. Strained alkenes are known to rearrange to carbenes at high temperatures.¹² Compound **6** has two possibilities for such a reaction; one seems to be a cul-de-sac, but the other goes straight to carbene **7**, and then to **4**. This mechanism correctly predicts the fate of the ^{13}C label (dots in Scheme 5).

A second labeling experiment, this time with deuterium, is consistent with this process but reveals that even more is going on. It also yields valuable insight into the source of naphthalene. 1-Indanone can be exchanged at the α position by a modification ($\text{D}_2\text{O}/\text{NaOD}$, not $\text{D}_2\text{O}/\text{K}_2\text{CO}_3$) of the procedure of Lustig and Ragelis¹³ to give 2,2-dideuterio-1-indanone. Condensation with Meldrum's acid leads to **2-d₂**. Pyrolysis at $640\text{ }^{\circ}\text{C}$ and 0.005 Torr led to methyleneindene **4-d₂** labeled as indicated in Scheme 6. The mechanism shown above would place all of the deuterium in the *exo*-methylene position. Therefore, approximately one-half of the reaction takes another path, not revealed by the carbon label.

It would appear that some competitive, but slower, process renders the two methylene positions of **5** and **6** equivalent. The following Scheme 7 accomplishes that end through the intermediacy of 1,2-dimethylenebenzocyclobutene (**8**). The carbon label remains in the experimentally observed positions in this

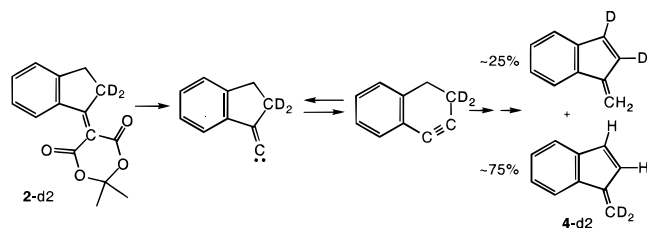
(10) Tseng, J.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 5474.

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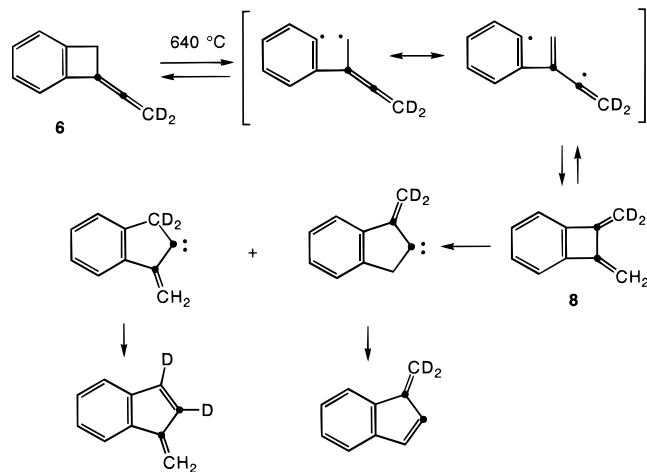
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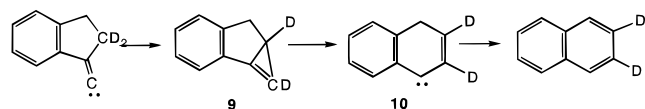
Scheme 6



Scheme 7



Scheme 8



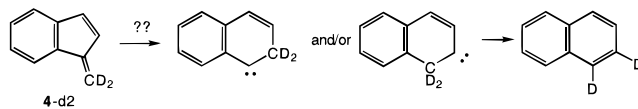
process (dots). The proposed mechanism finds excellent precedent in the thermal conversion of 3,4-dimethylenecyclobutene to fulvene and benzene at 620 °C in a ratio of 2:1.¹⁴ 1,2-Dimethylenebenzocyclobutene itself has not been so well studied but has been reported to rearrange to naphthalene when heated at 700 °C over a Nichrome wire.¹⁵

The naphthalene is labeled with deuterium in both the α and β positions. ¹³C also winds up in the α and β positions in the approximate ratio 1:2. Thus naphthalene cannot be formed from **4**, in which the label is equally distributed between two positions. This surmise is born out by control experiments, which show that only about 5% of naphthalene is formed from **4** under our reaction conditions. The plethora of potential routes to naphthalene makes mechanistic speculation difficult, but here are our thoughts on the likely mechanistic pathways. The vinylidene intermediate can insert into an adjacent position to give a fused cyclopropene **9**. Opening of the cyclopropene ring to a vinylcarbene, a common occurrence,¹² leads to **10** and thence to naphthalene labeled exclusively in the β position (Scheme 8). Cyclohexyne itself is thought to find its way to 1,3-cyclohexadiene by a parallel pathway.¹⁰

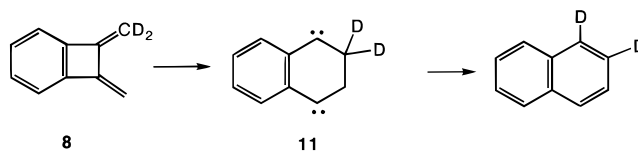
Some α -substituted naphthalene can be produced by the rearrangement of **4-d₂**, but this pathway can account only for very small amounts as we have shown through control experiments that only about 5% of **4** is converted into naphthalene under our reaction conditions (Scheme 9).

We suggest that the α -substituted material must come from the intermediate **8**, formed reversibly from **6**. Once the two

Scheme 9



Scheme 10



methylene groups are symmetrized through **8**, the naphthalene skeleton is in place and accessible, as is implied by the known conversion to naphthalene at 700 °C over Nichrome.¹⁵ We do not know the details, and dicarbene **11** is drawn as a convenience, but any route to naphthalene from **8** must lead to an α,β -substituted naphthalene (Scheme 10).

Despite these quite remarkable sequences, we have not found any evidence for our strained acetylene acting in dicarbene-like fashion. It may be that our choice was foolish, as the cyclohexyne intermediate **1** had a ready escape route built in, the reverse Diels–Alder reaction. It remains to be seen if the carbene-like behavior will appear once this escape route is cut off. We are pursuing two experiments of this kind and working out the details of the mechanism of naphthalene formation using labeled carbenes.

Experimental Section

General Procedure. Unless otherwise specified, all reagents were purchased from commercial suppliers (Aldrich or as specified) and used without further purification. ¹H and ¹³C NMR spectra were recorded with JEOL GSX-270, GE QE-300, and Varian Unity Inova 500 spectrometers. GC–MS analyses were carried out on a Hewlett-Packard 5890/5971 gas chromatograph equipped with a mass-selective detector on a 0.25-mm-i.d., 0.25-mm film thickness, 30-m HP-1701 capillary column. Precise masses were measured on a KRATOS MS 50 RFA high-resolution mass spectrometer. Temperatures were measured with a thermocouple or a thermometer and are uncorrected.

2,2-Dimethyl-5-(1'-indanylidene)-1,3-dioxane-4,6-dione (2). The synthesis follows the general method of Baxter and Brown.^{7a} A solution of 11 mL of TiCl₄ (100 mmol) in 25 mL of CCl₄ was added dropwise to dry tetrahydrofuran (190 mL) at 0 °C. A solution of 6.6 g of indanone (50 mmol) and 7.2 g of Meldrum's acid (50 mmol) in dry tetrahydrofuran (25 mL) was added slowly to the yellow precipitate and was followed by 16 mL of pyridine (250 mmol) in dry tetrahydrofuran (25 mL). The flask was then rinsed with an additional 60 mL of dry tetrahydrofuran. The ice bath surrounding the reaction vessel was allowed to warm to room temperature. The reaction was then stirred for 4 days, during which time the solution turned opaque slate grey. Water and ether were added until the solid dissolved, and the aqueous layer was removed. The organic layer was washed with H₂O (1 L), saturated NaCl solution (300 mL), saturated NaHCO₃ (600 mL), and H₂O again (600 mL). It was dried over NaSO₄, and the solvents were evaporated at the water pump. The crude product was then recrystallized from ethanol, yielding 4.2 g of white needles, 3 g of which was redissolved in ether and chromatographed on a silica gel column with 5:1 pentane:ether solvent. A second recrystallization from ethanol yielded 0.4 g (2.6 mmol, 7.3%): mp 101–108 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.79 (s, 6H), 3.15 (t, J = 5.2 Hz, 2H), 3.60 (t, J = 5.2 Hz, 2H), 7.46 (d, J = 7.5 Hz, 1H), 7.53 (m, 1H), 8.68 (d, J = 8.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 27.10, 30.54, 36.91, 103.49, 109.61, 125.62, 127.03, 129.76, 134.45, 137.08, 155.75, 162.33, 163.56, 178.29; IR (KBr) cm⁻¹ 1720, 1559, 1293, 1201; MS-EI m/z (relative intensity) 258 (3), 200 (100), 172 (39), 156 (98), 128 (94); HRMS calcd for C₁₅H₁₄O₄ 258.0892, found 258.0870.

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2,2-Dimethyl-5-(1'-indanylidene)-[5-¹³C]-1,3-dioxane-4,6-dione. This compound was synthesized in a fashion similar to that for **2**, except that **2** equiv of 1-indanone was used. The yield was 36.5%: ¹³C NMR (67.94 MHz, CDCl₃) δ 109.6

2,2-Dimethyl-5-[5-¹³C]-1,3-dioxane-4,6-dione. This compound was synthesized through a modification of the method of Davidson and Bernhard.¹⁶ [2-¹³C]Malonic acid (Cambridge, 0.34 g, 3.26 mmol) and isopropenyl acetate (0.38 mL, 3.45 mmol) were placed into a 5-mL round-bottomed flask equipped with a magnetic stirring bar and cooled in an ice bath to 0 °C. To the mixture was added one drop of concentrated sulfuric acid, and stirring was continued at 0 °C for 2 h. The solution was cooled in the refrigerator overnight and filtered, and the solid was washed with 2 × 5 mL of cyclohexane. The crude solid (0.42 g) was dissolved in methylene chloride. Filtration led to 0.13 g of a solid containing mainly malonic acid and 2,2-dimethyl-[5-¹³C]-1,3-dioxane-4,6-dione. Evaporation of the methylene chloride layer gave 0.32 g of 2,2-dimethyl-[5-¹³C]-1,3-dioxane-4,6-dione (68%): ¹H NMR (270 MHz, CDCl₃) δ 1.79 (s, 6H), 3.63 (d, *J* = 133.7 Hz, 2H); ¹³C NMR (67.94 MHz, CDCl₃) δ 36.4 (s) (48 scans of a dilute sample).

2,2-Dideuterio-1-indanone. This compound was synthesized according to a modification of the method of Lustig and Ragelis,¹³ in which NaH was used as the base. 1-Indanone (2.0 g, 15.0 mmol), deuterium oxide (10 mL, 500 mmol), NaH (0.20 g, 8.3 mmol), and dioxane (10 mL) were used in the reaction. A 70% yield of 2,2-dideuterio-1-indanone was obtained: ¹H NMR (270 MHz, CDCl₃) δ 2.62 (m, 0.06H), 3.10 (s, 2H), 7.3 (t, 1H), 7.41 (d, 1H), 7.55 (t, 1H), 7.70 (d, 1H).

2,2-Dimethyl-5-(2',2'-dideuterio-1'-indanylidene)-1,3-dioxane-4,6-dione. This compound was synthesized in a yield of 35% in a fashion similar to that for **2**, except that deuterium oxide was used instead of water in the workup: ¹H NMR (270 MHz, CDCl₃) δ 3.15 (m, 2H), 3.60 (m, 0.5H); other signals are the same as in the unlabeled compound.

Typical Procedure for Pyrolysis. Pyrolyses were carried out in a 500-mL two-necked quartz flask wrapped with heating wire. One of the necks was connected to a 10-mL round flask into which the corresponding starting material was placed; the other neck was connected to a liquid nitrogen trap which was in turn connected to a vacuum system. Prior to the pyrolysis, the quartz flask was heated to the desired temperature and the whole system was evacuated for at

least 1 h. The starting material was slowly dropped into the quartz flask in such a way that the pressure did not exceed 60 × 10⁻³ Torr. After the pyrolysis was completed, the products in the cold trap were immediately dissolved in an appropriate solvent for analysis or further treatment.

Pyrolysis of 2,2-Dimethyl-5-(1'-indanylidene)-1,3-dioxane-4,6-dione (2). Compound **2** (84 mg, 0.325 mmol) was pyrolyzed to give the products as a yellow oil. An analysis (GC) of the products revealed methyleneindene (**4**) (0.2 mmol, 66%) and naphthalene (0.1 mmol, 26%) as the major products, along with a very small amount of unidentified compounds whose *m/z* values were 128 and 116.

Pyrolysis of 2,2-Dimethyl-5-(1'-indanylidene)-[5-¹³C]-1,3-dioxane-4,6-dione. The ¹³C content of the products was measured by comparing the corresponding signal intensities to those from the products of the experiment using unlabeled material. The ¹H (500 MHz) signal of unlabeled **4** [δ 6.47 (dd, *J* = 5.0, 5.0 Hz, 1H)] was split into a wide doublet in the ¹³C-containing material [δ 6.47 (d, *J* = 5.0, 170 Hz, 0.5H)]. The residual ¹H of unlabeled material appeared as usual at δ 6.47 (0.5H).

Pyrolysis of 2,2-Dimethyl-5-(2',2'-dideuterio-1'-indanylidene)-1,3-dioxane-4,6-dione (2). Pyrolysis led to deuterated naphthalene and methyleneindene. Naphthalene: ¹H NMR (500 MHz) δ 7.8 (m, 1H), 7.40 (m, 1H); ²H NMR (500 MHz) δ 7.8 (s), 7.40 (s); GC-MS *m/z* (relative intensity) 131 (10), 130 (95), 129 (100). Methyleneindene: ¹H NMR (500 MHz) δ 6.47 (m, 0.75H), 6.03, 6.02 (0.5H),¹⁷ 5.68 (s), 5.7 (s)¹⁷ (0.5H); ²H NMR (500 MHz) (relative intensity) δ 6.84 (s, 0.25H), 6.48 (s, 0.25H), 6.0 (s, 1H), 6.03 (s, 1H); GC-MS *m/z* (relative intensity) 131 (10), 130 (100), 129 (95).

Pyrolysis of 3,4-Dihydro-1,2-naphthalic Anhydride (3). Compound **3** (60 mg, 0.30 mmol) was pyrolyzed as described above to give methyleneindene (**4**) in 20% yield (0.06 mmol) and naphthalene in 17% yield (0.05 mmol) along with a very small amount of starting material. The determination of yield was by ¹H NMR spectroscopy.

Acknowledgment. We thank the National Science Foundation for support of this work through Grant CHE-9702823. We also thank Dr. Wei Wang for valuable assistance in obtaining NMR spectra.

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(17) The multiple signals result from different deuterated isomers of **4**.