the resonance interaction at the transition structure corresponding to the concerted synchronous process is about one-half (from symmetry considerations since RR is present) its value for the asynchronous one-bond process (where the RR element is not present). In common with the Woodward-Hoffmann approach, one expects that arguments based on symmetry will still hold when the system is perturbed slightly by functional group substitution.

In all our calculations on two-step reactions,[6,9] the diradical intermediate with one bond formed lies on a surface that is dominated by the same product-like diabatic surface as the final cyclic product, and thus, the second barrier to form products is very small.

Of course there is a great debate on the synchronous vs. nonsynchronous nature of cycloadditions (see the discussion in ref 1). We have treated only three examples numerically in this paper. These examples have been chosen because the topology of the potential surfaces is reliably documented at the MC-SCF level where the diradical one-bond transition structure can be determined with the same accuracy as the transition structure for the synchronous path. While the calculations reported in this work have been carried out at the STO-3G level (for reasons of economy), in all of the cases studied the preference for concerted/nonconcerted pathways at the 4-31G is correctly reproduced at the STO-3G level. Thus, while basis set effects appear to be very important in determining the stability of the products relative to the reactants and the barrier heights (see ref 9, for example), the relative energies of the concerted and nonconcerted transition structures appear to be reliable at the STO-3G level. Thus, for these examples, the qualitative arguments of section 2 of this paper have withstood the test of numerical computation.

Finally, we should point out that arguments based upon diabatic surface intersections do not guarantee that the transition structure for one or the other of the possible pathways actually exists. Thus, for ethylene cycloaddition, the minimum and transition structures for the one-bond nonconcerted process virtually disappear for this preferred mechanism. similarily, on the basis of the symmetry arguments presented previously, the one-bond mechanism for the Diels-Alder reaction should be preferred since the RR symmetry element (a reflection plane) is present for the synchronous approach. However, at the MC-SCF 4-31G level no transition structure exists[15] for the one-bond mechanism. In other words, the existence of a minimum of a diabatic surface crossing does not imply that the saddle point surface of the transition structure will actually be formed when the resonance interaction is "switched on". This fact is also demonstrated in the example of the addition of CO to H_2 considered in this work.

In conclusion, we believe that the present results indicate that, while the electronic origin of the reaction barrier[6-9] can be understood from a knowledge of the diabatic surface intersections alone, the resonance interaction plays the dominant role in discriminating between concerted synchronous two-bond and concerted/nonconcerted one-bond reaction mechanisms since the diabatic surfaces for the possible competing mechanisms intersect at similar values of the energy.

Acknowledgment. This work has been supported in part from Grant GR/D/23305 from the Science and Engineering Council of the U.K. and by the EEC under Contract ST2-0083-2-UK.

Registry No. CO, 630-08-0; acetylene, 74-86-2; fulminic acid, 506-85-4; ethylene, 74-85-1.

Thermal Isomerization of Benzocyclobutene

Orville L. Chapman,* Uh-Po Eric Tsou, and Jeffery W. Johnson

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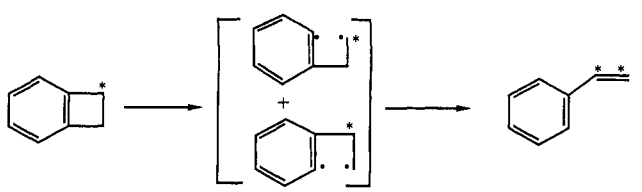
Abstract: Thermolysis of benzocyclobutene ($^{13}CH_2$, 99%) gives styrene labeled in the β (48%), ortho (30%), α (14%), meta (4%), and para (4%) positions. The major labels (β and ortho) are consistent with a mechanism involving interconversions of the isomeric tolylmethylenes and the methylcycloheptatetraenes. This mechanism also involves interconversion of *o*-tolylmethylene with *o*-xylylene and *p*-tolylmethylene with *p*-xylylene. A minor mechanism produces 25% of the styrene. This mechanism involves cleavage of the aryl carbon to the methylene carbon bond in benzocyclobutene followed by hydrogen transfer to produce styrene. Thermolysis of *p*-xylylene produced from [2.2]paracyclophane gives styrene (55%), *p*-xylene (31%), benzocyclobutene (4%), benzene (4%), and toluene (3%). Thermolysis of [2.2]metacyclophane gives styrene (18%), *p*-xylene (25%), *m*-xylene (3%), benzocyclobutene (1%), benzene (7%), and toluene (22%).

The thermal isomerization of benzocyclobutene to styrene[1] provides an interesting mechanism problem. The simplest mechanism for this process involves homolysis to a diradical followed by hydrogen transfer (mechanism I). An alternative, mechanism II, involves the interconversions of the tolylmethylenes and methylcycloheptatetraenes established by matrix isolation studies.[2] This mechanism also explains the thermolysis (150 °C) of *o*-tolyldiazomethane to benzocyclobutene and styrene reported by Vander Stouw and Shechter[3] and the thermolysis (420 °C) of *m*- and *p*-tolyldiazomethanes to benzocyclobutene and styrene reported by Baron et al.[4] Mechanism II is consistent with the ^{13}C-labeling experiment of Hedaya and Kent[5] (eq 1) and with the ^2H-labeling experiment of Vander Stouw et al. (eq 2).[6]

mechanism I



* = ^{13}C

(1) (a) Baron, W. J.; DeCamp, M. R. *Tetrahedron Lett.* **1973**, 4225-4228. (b) Cava, M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266-4268.

(2) (a) Chapman, O. L.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 7973-7974. (b) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984; Chapter 4.

(3) Vander Stouw, G. G. Ph.D. Dissertation, Ohio State University, Columbus, OH, 1964.

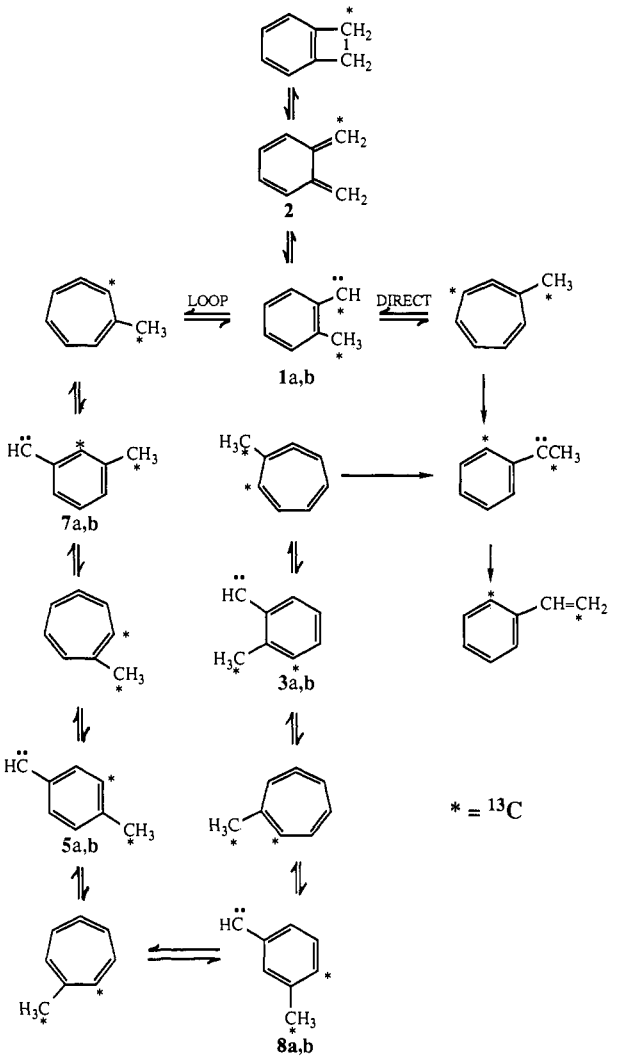
(4) Baron, W.; Jones, M., Jr.; Gaspar, P. *J. Am. Chem. Soc.* **1970**, *92*, 4739-4740.

(5) Hedaya, E.; Kent, M. *J. Am. Chem. Soc.* **1971**, *93*, 3283-3285.

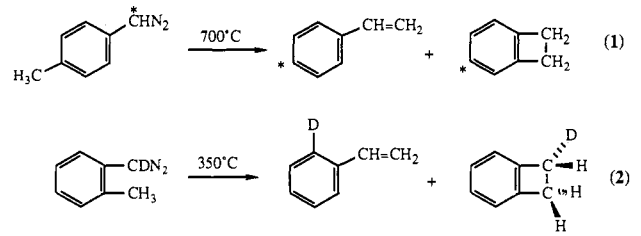
(6) Shechter, H.; Vander Stouw, G. G.; Kraska, A. R. *J. Am. Chem. Soc.* **1972**, *94*, 1655-1661.

0002-7863/87/1509-0553$01.50/0

mechanism II



Mechanisms I and II can be distinguished by ^{13}C labeling[7a] or by deuterium labeling.[7b] We describe now the ^{13}C-labeling experiment. Trahanovsky and Schribner[7b] have done the deuterium-labeling experiment. Methylene-labeled (^{13}C) benzocyclobutene should give equal amounts of styrene labeled in the α and β positions by mechanism I. Mechanism II predicts equal amounts of styrene labeled in the β and ortho positions.



Results and Discussion

The reaction sequence in Scheme I provides methylene-labeled (99% ^{13}C) benzocyclobutene. Thermolysis (930 °C, 0.1 torr, quartz tube packed with quartz chips) of labeled benzocyclobutene gives a product with the ^{13}C NMR spectrum shown in Figure 1. Only labeled carbons are visible in this spectrum.[8] The styrene has major labels[9,10] in the β (48 ± 2%) and ortho (30 ± 2%)

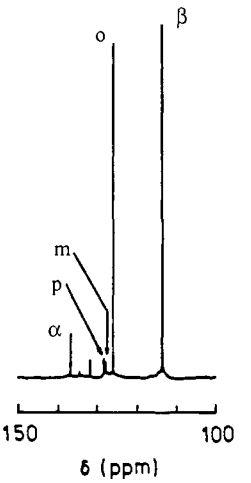
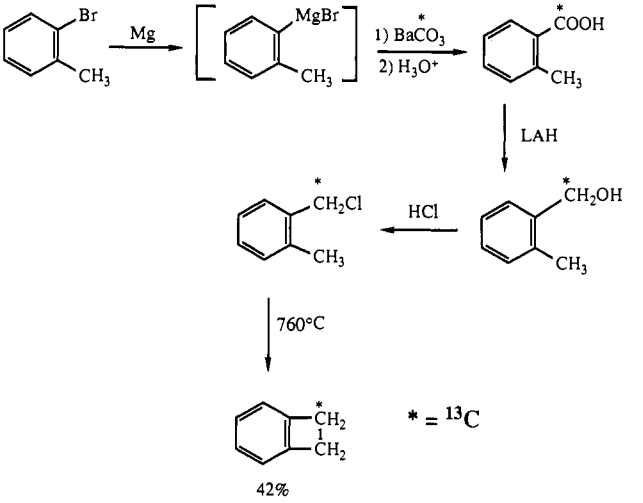
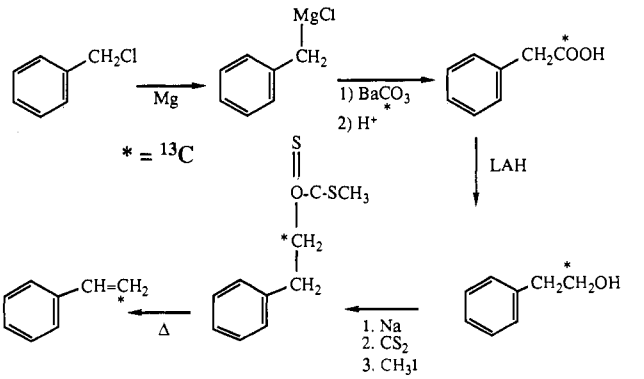


Figure 1. ^{13}C NMR spectrum of crude product from thermolysis of methylene-labeled benzocyclobutene (99% ^{13}C). Only labeled positions are visible. Labeled styrene positions are β (113.34), ortho (125.82), α (136.54), meta (128.31), and para (127.79). The origin of the peak at 131.92 is not known. Traces of ^{13}C-methyl-labeled *o*- and *p*-xylene are observed at higher field.

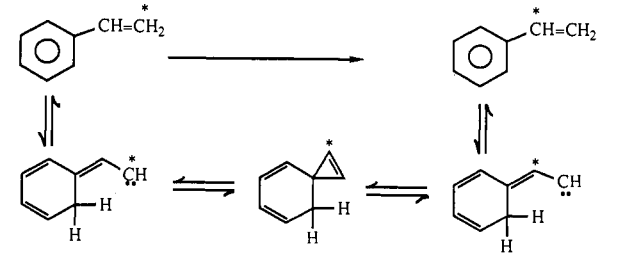
Scheme I



Scheme II



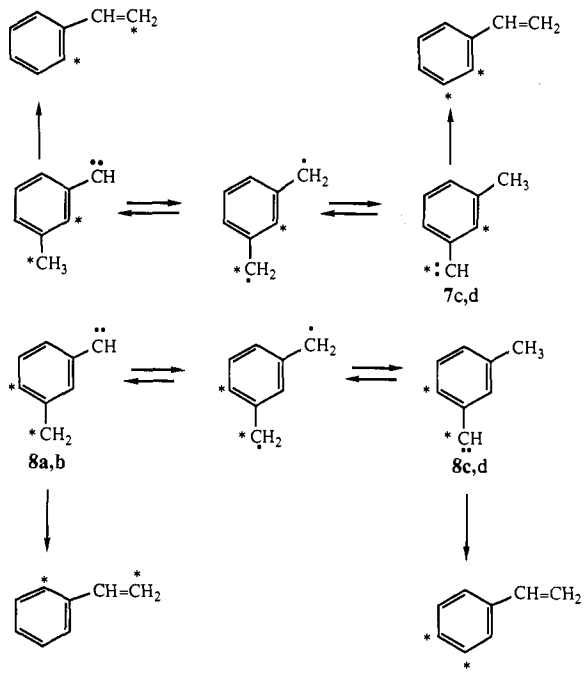
Scheme III



(7) (a) Chapman, O. L.; Tsou, U. E. *J. Am. Chem. Soc.* **1984**, *196*, 7974–7976. (b) Trahanovsky, W. S.; Schribner, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7976–7978.

(8) A standard ^{13}C NMR spectrum of unlabeled styrene under the same condition (solvent, concentration, and instrumental parameters) gave no visible resonances.

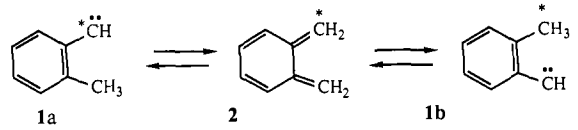
Scheme IV



positions with minor labels in the α (14 ± 2%), meta (4 ± 2%), and para (4 ± 2%) positions. Mass spectrometry shows only monolabeled styrene. The product (72% recovery) contains styrene (96%), *p*-xylene (1%), *o*-xylene (1%), and benzocyclobutene (2%).[11] The observation of major labels in the ortho and β positions of styrene is not consistent with mechanism I, but it is consistent with mechanism II. The inequality of the label in the β and ortho positions requires that the minor labels arise principally at the expense of the ortho label, i.e., the sum of the ortho, α, meta, and para labels must equal the β label. The origin of the minor labels is thus of substantial interest.

The α-labeled styrene has at least two origins. A small portion (<4%) of the α label comes from rearrangement of β-labeled styrene. Thermolysis (930 °C, 0.1 torr) of β-labeled (^{13}C, 99%) styrene prepared as shown in Scheme II gives α-labeled styrene (4% by ^{13}C NMR). The rearrangement of β-labeled to α-labeled styrene may occur as shown in Scheme III. The major portion of the α-labeled styrene from the thermal isomerization of labeled benzocyclobutene, however, probably arises via mechanism I. This mechanism predicts equal amounts of α and β labels, which differs from the prediction (ortho and β) of mechanism II. If mechanism I competes with mechanism II, the amount of ortho label observed should be less than 50%, and the β label should be 50%. This prediction is consistent with the experimental results. The participation of mechanism I limits the amount of ortho label observed. Approximately 25% (14% × 2 less the correction for $\beta \rightarrow \alpha$ rearrangement) of the styrene must be formed via mechanism I to account for the α (14 ± 2%), β (48 ± 2%), and ortho (30 ± 2%) labels observed. The remaining 75% of the styrene is formed by mechanism II. (A blend of mechanisms I and II accounts for the major labels, but the minor meta and para labels pose a separate problem.) Before dealing with this problem, we must consider the interconversion of *o*-tolylmethylene and *o*-xylylene.

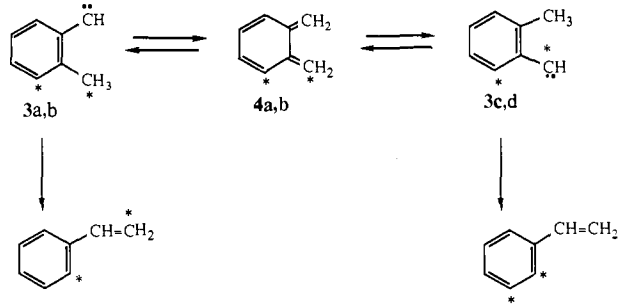
Conversion of *o*-tolylmethylene (**1**) to *o*-xylylene (**2**) occurs photochemically or thermally in an argon matrix.[2] The thermal reaction in argon proceeds at an easily measurable rate at 4.6 K.[34]



1a **2** **1b**

The high-temperature reverse reaction accounts for the label rearrangement, and it provides the entry to the tolylmethylenes from benzocyclobutene. Benzocyclobutene is not converted to styrene at temperatures below 770 °C,[1] but it equilibrates with *o*-xylylene at much lower temperatures.[11] The conversion of *o*-xylylene to *o*-tolylmethylene thus has the highest barrier between benzocyclobutene and styrene. This conversion has significance in the formation of the meta and para labels.

Mechanism II has a direct path from benzocyclobutene to styrene and a loop, which also leads to styrene. The direct path and the loop diverge at *o*-tolylmethylene (**1**). The ^{13}C label follows a different path in the loop, but it gives the same labeled styrenes as the direct path except for the small fraction that rearranges through *o*-tolylmethylene again. The new *o*-tolylmethylenes (**3a,b**)



in the loop are labeled differently. Interconversion with *o*-xylylene (**4a,b**) leads to further label rearrangement. The rearranged *o*-tolylmethylenes (**3c,d**) lead ultimately to ortho- and meta-labeled styrenes. This process accounts for meta-labeled styrene, but it has no explanation for the formation of para-labeled styrene. Could similar rearrangements of *m*-tolylmethylene and *p*-tolylmethylene occur? If so, *m*-xylylene and *p*-xylylene should give styrene at high temperatures.

This hypothesis was most easily tested for *p*-xylylene. Thermolysis (930 °C, 0.1 torr) of [2.2]paracyclophane, which is known to give *p*-xylylene[12] at lower temperatures, gives styrene (55%), *p*-xylene (31%), benzene (4%), toluene (3%), and benzocyclobutene (4%), with a total mass recovery of 54%. The formation of benzocyclobutene and styrene suggests that *p*-xylylene equilibrates with *p*-tolylmethylene, which subsequently rearranges as shown in Mechanism II. The relatively large amount of *p*-xylene suggests that the small amounts of *o*-xylene and *p*-xylene observed in the thermolysis of benzocyclobutene may arise from reduction of *o*-xylylene and *p*-xylylene. Thus, the interconversion of *p*-xylylene and *p*-tolylmethylene must now be considered as a source of para-labeled styrene. The interconversion of *p*-tolylmethylenes with the corresponding *p*-xylylenes **6a,b** gives rearranged *p*-tolylmethylenes **5c,d**, which lead ultimately to meta-labeled and para-labeled styrene. Two sets of *m*-tolylmethylenes (**7a,b** and **8a,b**) are generated in the loop of mechanism II. Label rearrangement via the corresponding *m*-xylylenes gives **7c,d**, which lead to ortho- and meta-labeled styrenes, and **8c,d**, which also lead to meta- and para-labeled styrenes. The possibility of interconversion of *m*-xylylene and *m*-tolylmethylene is supported by thermolysis of [2.2]metacyclophane. Thermolysis (930 °C, 0.1 torr) of [2.2]metacyclophane[32] gives styrene (18%), *p*-xylene (35%), *m*-xylene (3%), benzocyclobutene (1%), benzene (7%), and toluene (22%), with a total mass recovery of 56%. The thermolysis of [2.2]metaparacyclophane also gives benzocyclobutene (1%), styrene (10%), benzene (3%), *p*-xylene (63%),

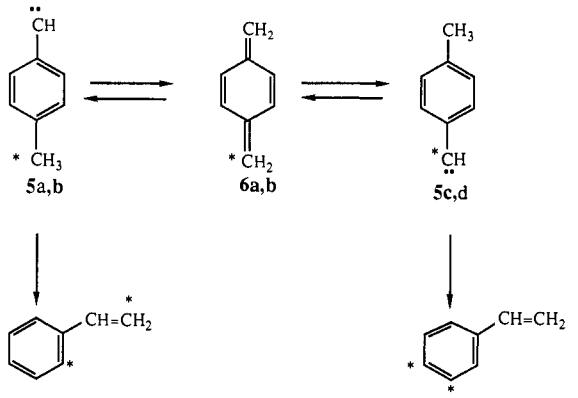
(9) The percentage labels measured by integration for the ^{13}C-labeled products were corrected for the relative intensity of the various carbons of unlabeled styrene in the same solvent and concentration and using the same instrumental parameters. The relative intensities were β, 0.66; α, 0.27; ortho, 1.00; meta, 0.47; and para, 0.29.

(10) (a) ^{13}C NMR spectrum from Sadtler Research Laboratories, Inc., compound No. 4006C. (b) Stothers, J. B.; Dhami, K. S. *Can. J. Chem.* **1965**, *43*, 510–520.

(11) Roth, W. R.; Bierman, M.; Dekker, H.; Jochems, R.; Mosselman, C.; Hermann, H. *Chem. Ber.* **1978**, *111*, 3982–3903.

(12) (a) Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970**, *92*, 1436–1438. (b) Pearson, J. M.; Six, H. A.; Williams, D. J.; Levy, M. *J. Am. Chem. Soc.* **1971**, *93*, 5034–5036.

(13) Anderson, J. L. U.S. Patent 2756239, 1956.



m-xylene (1%), and toluene (15%), with a total mass recovery of 61%. The loop in mechanism II must represent approximately 8 ± 4% of the reaction proceeding via Scheme IV to account for the meta (4 ± 2%) and para (4 ± 2%) labels.

Based on matrix isolation studies,[2,34] mechanism II is a permissible mechanism for the thermal isomerization of benzocyclobutene to styrene because the lowest singlet excited states of arylmethylenes are only a few kilocalories/mole above the triplet ground state,[14] and thermal population is significant even at room temperature. Calculations place singlet tropylidene about 15 kcal/mol above cycloheptatetraene,[15] and this state is populated significantly at high temperatures, as are the triplet states of the xylylenes. It is thus reasonable to compare the photochemical processes with those observed at high temperatures.

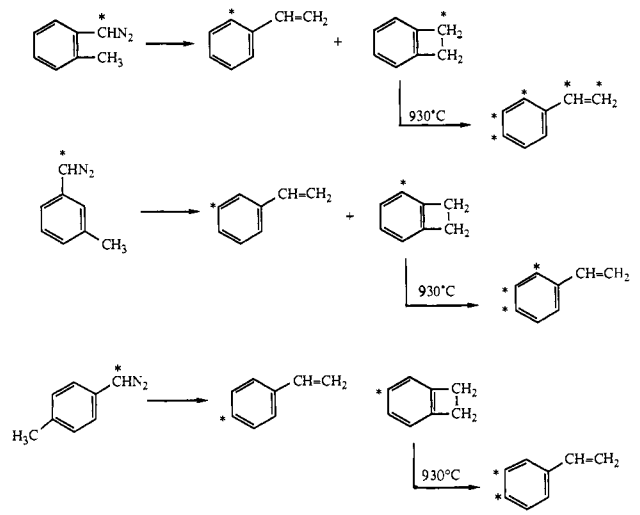
It is possible in principle to show that tolylmethylenes equilibrate with the corresponding xylylenes by thermal rearrangement of appropriately labeled tolylmethylenes at 930 °C. Thermolyses of the isomeric tolyldiazomethanes ^{13}C labeled (99%) in the diazomethyl group give the results shown in Table I. Only *o*-tolyldiazomethane gives label distribution in all positions other than the ipso position. The problem lies in the fact that the diazo compounds decompose giving styrene and benzocyclobutene long before they reach the high-temperature zone (930 °C) required for equilibration of the tolylmethylenes and the xylylenes. The *o*-tolydiazomethane decomposes to ortho-labeled styrene (cf. the deuterium-labeling experiment, ref 6) and methylene-labeled (^{13}C) benzocyclobutene, which is converted to styrene with the expected labeling pattern in the 930 °C zone. The benzocyclobutene from *m*-tolyldiazomethane and *p*-tolyldiazomethane gives the products expected (Scheme V). Evidence that *p*-tolylmethylene equilibrates with *p*-xylylene when formed at high temperatures[13] comes from the thermolysis (930 °C) of labeled *p*-ethyltoluene (99% ^{13}C in aromatic methyl group, Scheme VI). This thermolysis gives styrene labeled in all positions except the ipso position (Table I, Scheme VII). Formation of *p*-tolylmethylene from *p*-ethyltoluene occurs only at high temperatures (810 °C).[1] This temperature is required to break the bonds necessary to form *p*-tolylmethylene.

The labeling experiments described and the deuterium-labeling results of Trahanovsky and Schribner[7] are consistent with a competition between mechanism I (25%) and mechanism II (75%). These results alone, however, do not require that one discard the mechanisms originally suggested by Vander Stouw and Shechter[3] and by Baron et al.[4] These results do require the addition of mechanism I or an equivalent mechanism and the equilibration of *o*-tolylmethylene, *p*-tolylmethylene, and *m*-tolylmethylene with the corresponding xylylenes. The chemistry of mechanism II is established securely by our matrix experiments, and we interpret our labeling results on this basis.

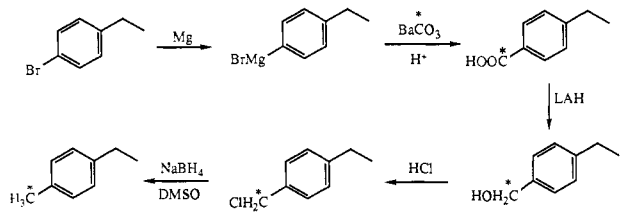
Conclusions

Two mechanisms compete in the conversion of benzocyclobutene to styrene. Mechanism I contributes approximately 25% of the styrene, and mechanism II contributes approximately 75% of the styrene. The interconversion of isomeric tolylmethylenes and the

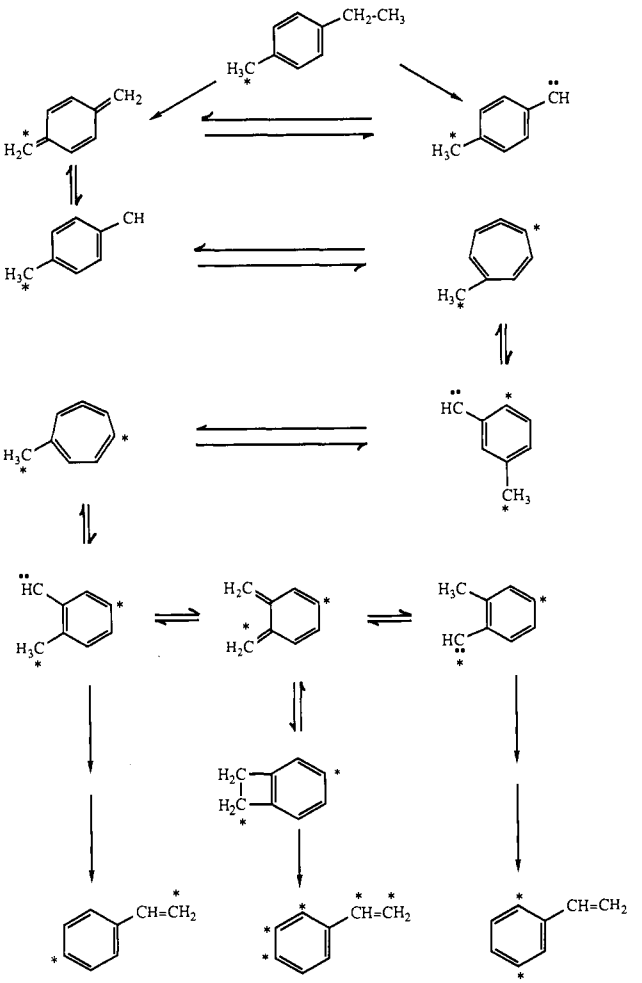
Scheme V



Scheme VI

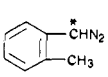
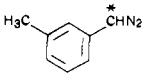
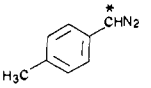
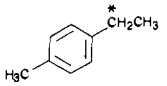


Scheme VII



(14) Trozzolo, A. M.; Wasserman, E. In *Carbenes*; Moss, R. A., Jones, M., Eds.; R. E. Kreiger: Malabar, FL, 1983; Vol. 2, Chapter 5.
(15) Schaefer, H. F., **III**; Radom, L.; Vincent, M. A. *Nouv. J. Chim.* **1980**, *4*, 411–415.

Table I. Labeled Styrenes from Various Precursors

labeled styrene	precursors,[a] %				
					d 
ortho	30	42	6	0	12
meta	4	4	80	17	19
para	4	6	14	83	29
α	14	11	0	0	27
β	48	37	0	0	13

[a] * = 99% ^{13}C.

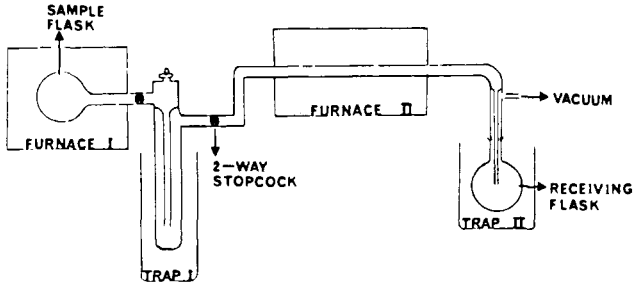


Figure 2. Apparatus for aryldiazomethane thermolysis.

corresponding xylylenes is established. The highest barrier between benzocyclobutene and styrene in mechanism II is the isomerization of *o*-xylylene to *o*-tolylmethylene.

Experimental Section

General Procedures. Thermolysis experiments used a $^1/_2$-in.-diameter quartz tube packed with quartz chips. An E. H. Sargent Co. 49090 tube furnace provided a 7-in. hot zone. A trap at 77 K retained products (Figure 2). Ambient-temperature NMR spectra were obtained on a Bruker WP-200 (200 MHz for ^1H, 50.22 MHz for ^{13}C), a Jeol FX-90Q (90 MHz for ^1H, 22.49 MHz for ^{13}C), or a Varian Associates T-60 (60 MHz for ^1H) spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane (Me_4Si). The UCLA Chemistry Department mass spectrometer facility provided high-resolution mass spectra (HRMS) and low-resolution mass spectra (LRMS) from an AEI-MS902 spectrometer. A Kratos-MS25 spectrometer with a 90-ft capillary column (DB-1 or SE-52) and a HP-5830 gas chromatograph with a 90-ft capillary column (SE-52) were used for supplied GC/MS analyses and GLC analyses, respectively. Melting points are uncorrected.

Materials. Barium carbonate (99% ^{13}C) purchased from Stohler Isotope Chemicals was used without further purification. Tetrahydrofuran was stored over potassium hydroxide and distilled from sodium. Dimethyl sulfoxide was distilled (30 torr) from calcium hydride. Other chemicals were purchased from Aldrich or Alfa and used as received.

[*carboxy*-^{13}C]-*o*-Toluic Acid.[16] *o*-Methylphenylmagnesium bromide was prepared from magnesium turnings (3.68 g, 153 mmol) and *o*-bromotoluene (13.13 g, 76.8 mmol) in anhydrous ether (60 mL). The procedure reported by Dauben et al.[16] gave [*carboxy*-^{13}C]-*o*-toluic acid (3.56 g, 26.0 mmol, 87%) from the Grignard solution and 99% ^{13}C barium carbonate (5.92 g, 29.8 mmol): mp 106–108 °C; ^1H NMR ($CDCl_3$) δ 2.65 (s, 3 H), 7.19–7.53 (m, 3 H), 8.00–8.12 (m, 1 H), 12.10 (br s, 1 H); mass spectrum (16 eV), *m/e* (relative intensity) 138 (10), 137 (100, M^+), 120 (7), 119 (54); ^{13}C NMR ($CDCl_3$) δ 173.48 (^{13}CO-OH).

***o*-Methyl[α-^{13}C]benzyl Alcohol.**[18] Dropwise addition of a solution of [*carboxy*-^{13}C]-*o*-toluic acid (1.36 g, 9.9 mmol) in anhydrous ether (25 mL) to a well-stirred solution of lithium aluminum hydride (2.28 g, 60 mmol) in anhydrous ether (50 mL) under nitrogen gave a cloudy solution. Reflux (3 h), cooling, treatment with saturated aqueous sodium sulfate solution, filtration, drying (Na_2SO_4), and concentration under reduced pressure gave *o*-methyl[α-^{13}C]benzyl alcohol (0.99 g, 8.1 mmol, 82%) as white solid: mp 34–37 °C; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H), 3.30 (br s, 1 H), 4.54 (d, 2 H, $J_{^{13}C\text{-}H\alpha}$ = 140 Hz), 7.10–7.35 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 63.26 ($^{13}CH_2OH$).

***o*-Methyl[α-^{13}C]benzyl Chloride.**[19] Neat *o*-methyl[α-^{13}C]benzyl alcohol (0.83 g, 6.7 mmol) reacted directly with 8.4 mL of concentrated hydrochloric acid at room temperature for 3 h, giving a white solution. Dilution with distilled water (10 mL), extraction with ether, washing with H_2O, drying (Na_2SO_4), and concentration under reduced pressure gave *o*-methyl[α-^{13}C]benzyl chloride (5.4 mmol, 81%) as a colorless liquid. Distillation (30 torr) gave *o*-methyl[α-^{13}C]benzyl chloride (0.69 g, 4.9 mmol, 73%) as a clear liquid: bp 97–98 °C [unlabeled, lit.[20] bp 95–96 °C/25 torr]; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 4.55 (d, 2 H, $J_{^{13}C\text{-}H\alpha}$ = 146 Hz), 7.10–7.30 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 44.50 ($^{13}CH_2Cl$).

[α-^{13}C]Benzocyclobutene.[19] Neat *o*-methyl[α-^{13}C]benzyl chloride (309.5 mg, 2.186 mmol), pyrolyzed at 760 °C (0.1 torr) via the method of Trahanovsky,[19] afforded 193.8 mg (1.846 mmol, 84%) of [α-^{13}C]-benzocyclobutene: bp 141–143 °C [unlabeled, lit.[20] bp 143 °C]; ^1H NMR ($CDCl_3$) δ 2.79–2.84 (m, 1 H), 3.13–3.19 (m, 2 H), 3.49–3.53 (m, 1 H), 6.95–7.39 (m, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 106 (9), 105 (100, M^+), 104 (49), 79 (15), 78 (17), M^+ calcd 105.0660, obsd 105.0655; ^{13}C NMR ($CDCl_3$) δ 29.71 ($^{13}CH_2$).

Thermolysis of [α-^{13}C]Benzocyclobutene. Neat [α-^{13}C]benzocyclobutene (115 mg, 1.10 mmol), thermolyzed at 930 °C (0.1 torr), afforded 81.5 mg of products. GLC and GC/MS analyses showed styrene (95.5%), starting material (2.0%), *o*-xylene (1.4%), and *p*-xylene (0.5%). The ^{13}C NMR ($CDCl_3$) spectrum (Figure 1) of the final products is assigned[10] as follows: δ 136.54 (α carbon of styrene), 128.31 (meta carbon of styrene), 127.79 (para carbon of styrene), 125.82 (ortho carbon of styrene), 113.34 (β carbon of styrene), 29.71 (α carbon of starting material), 21.03 (methyl carbon of *p*-xylene), and 19.29 (methyl carbon of *o*-xylene). The ^1H NMR spectra of the final products support these assignments. The origin of the peak at δ 131.92 is not known. A repeat experiment gave similar results within experimental error.

2-Phenyl[*carboxy*-^{13}C]acetic Acid. The procedure described for [*carboxy*-^{13}C]-*o*-toluic acid provided 2-phenyl[*carboxy*-^{13}C]acetic acid (3.40 g, 24.8 mmol, 83%) from benzyl chloride (9.72 g, 76.8 mmol), magnesium turnings (3.68 g, 153 mmol), and 99% ^{13}C barium carbonate (5.92 g, 29.8 mmol): mp 77–79 °C [unlabeled, lit.[22] mp 76–76.5 °C]; ^1H NMR ($CDCl_3$) δ 3.63 (d, 2 H, $J_{^{13}C\text{-}H\beta}$ = 8 Hz), 7.29 (s, 5 H), 11.35 (br s, 1 H); mass spectrum (16 eV), *m/e* (relative intensity) 138 (8), 137 (100, M^+), 119 (10), 92 (24), 91 (65), M^+ calcd 137.0559, obsd 137.0559; ^{13}C NMR ($CDCl_3$) δ 177.55 (^{13}COOH).

[α-^{13}C]Phenethyl Alcohol. The reduction procedure described for *o*-methyl[α-^{13}C]benzyl alcohol was applied to 2-phenyl[*carboxy*-^{13}C]acetic acid (1.0 g, 7 mmol), affording 0.85 g (6.9 mmol, 95%) of the ^{13}C-labeled alcohol as a colorless liquid: bp 105–107 °C/15 torr [unlabeled, lit.[23] bp 116–118 °C/25 torr]; ^1H NMR ($CDCl_3$) δ 1.69 (s, 1 H), 2.75–3.00 (m, 3 H), 5.07 (t, 1 H, $J_{H\alpha\text{-}H\beta}$ = 7 Hz), 7.19–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 63.30 ($^{13}CH_2OH$).

Xanthate Formation of [α-^{13}C]Phenethyl Alcohol.[24] [α-^{13}C]Phenyl alcohol (0.58 g, 4.7 mmol) was reacted with sodium (0.13 g, 6 mmol) in anhydrous ether (30 mL) at room temperature for 30 h under nitrogen. Freshly distilled carbon disulfide (3.0 mL, 50 mmol) was added to the solution. Reflux, treatment with freshly distilled methyl iodide (4.0 mL, 64 mmol), reflux (1 h), filtration, and concentration under reduced pressure gave crude ^{13}C-labeled xanthate (0.77 g, 3.6 mmol, 77%): ^1H

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NMR ($CDCl_3$) δ 2.48 (s, 3 H), 3.06 (dt, 2 H, $J_{^{13}C-H\beta}$ = 7, $J_{H\alpha-H\beta}$ = 7 Hz), 4.76 (dt, 2 H, $J_{^{13}C-H}$ = 151, J_{H-H} = 7 Hz), 7.24–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 73.70 ($^{13}CH_2O$). The crude product was used for the next step without purification.

[β-^{13}C]Styrene.[24] Crude ^{13}C-labeled xanthate (0.92 g, 4.3 mmol), after refluxing at 210 °C for 3 h and vacuum distillation (30 torr), gave [β-^{13}C]styrene (90 mg, 0.86 mmol, 20%) as a colorless liquid: bp 145–147 °C [unlabeled, lit.[26] bp 48 °C/20 torr]; ^1H NMR ($CDCl_3$) δ 5.28 (dd, 1 H, $J_{^{13}C-H\beta Z}$ = 160, $J_{H\alpha-H\beta Z}$ = 12 Hz), 5.74 (dd, 1 H, $J_{^{13}C-H\beta E}$ = 160, $J_{H\alpha-H\beta E}$ = 18 Hz), 6.71 (dd, 1 H, $J_{H\alpha-H\beta E}$ = 18, $J_{H\alpha-H\beta Z}$ = 12 Hz), 7.05–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 113.34 (β carbon).[10]

Thermolysis of [β-^{13}C]Styrene. Neat [β-^{13}C]styrene (30 mg, 0.29 mmol), thermolyzed under exactly the same conditions as the pyrolysis of [α-^{13}C]benzocyclobutene, afforded 25 mg of products: ^{13}C NMR ($CDCl_3$) δ 136.54 (this peak was not observed in the starting material with the same concentration and instrumental parameters; α carbon of styrene),[10] 113.34 (β carbon of styrene). GLC and GC/MS analyses yielded styrene (99%) and benzene (1%).

[*carbaldehyde*-^{13}C]-*o*-Tolualdehyde.[26] Ceric ammonium nitrate (8.70 g, 15.9 mmol) in 16 mL of water was added dropwise to a warm solution (40 °C) of *o*-methyl[α-^{13}C]benzyl alcohol (0.93 g, 7.6 mmol) in 16 mL of water and stirred at 40–50 °C, giving a pale-yellow solution. Cooling, extraction with ether (3 × 10 mL), washing with saturated aqueous sodium carbonate solution (4 × 5 mL), drying (Na_2SO_4), filtration, and concentration under reduced pressure gave the ^{13}C-labeled aldehyde (0.91 g, 7.5 mmol, 99%) as a light-yellow liquid: bp 198–199 °C [unlabeled, lit.[27] bp 68–72 °C/6 torr]; ^1H NMR ($CDCl_3$) δ 2.64 (s, 3 H), 7.16–7.90 (m, 4 H), 10.42 (d, 1 H, $J_{^{13}D-H\alpha}$ = 174 Hz).

[*carbaldehyde*-^{13}C]-*o*-Tolualdehyde Tosylhydrazone. A warm solution (40 °C) of *p*-toluenesulfonohydrazide (1.41 g, 7.6 mmol) in 15 mL of absolute ethanol was treated with [*carbaldehyde*-^{13}C]-*o*-tolualdehyde (0.91 g, 7.6 mmol) and stirred at room temperature for 4 h, giving a yellow solution. Concentration under reduced pressure and recrystallization (chloroform/heptane) gave the ^{13}C-labeled tosylhydrazone (1.79 g, 6.2 mmol, 82%): mp 140–142 °C [unlabeled, lit.[28] mp 143–144 °C]; ^1H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 2.39 (s, 3 H), 7.14–7.33 (m, 6 H), 7.88 (d, 2 H, J_{H-H} = 8 Hz), 8.04 (d, 1 H, $J_{^{13}C-H}$ = 160 Hz), 8.25 (br s, 1 H); mass spectrum (16 ev), *m/e* (relative intensity) 290 (1), 289 (12, M^+), 156 (10), 134 (20), 133 (57), 105 (100), M^+ calcd 289.0966, obsd 289.0994; ^{13}C NMR ($CDCl_3$) δ 147.23 (^{13}C=N).

Sodium Salt of [*carbaldehyde*-^{13}C]-*o*-Tolualdehyde Tosylhydrazone. A solution of [*carbaldehyde*-^{13}C]-*o*-tolualdehyde tosylhydrazone (0.28 g, 1.0 mmol) in 15 mL of anhydrous tetrahydrofuran was treated with 0.05 g (1.0 mmol) of 50% sodium hydride in oil to give a cloudy solution. Stirring (30 min) at room temperature, diluting with petroleum ether (150 mL), filtering under nitrogen, washing the salt with petroleum ether, drying in vacuo (2 h), grinding, and drying in vacuo at 50 °C (overnight) gave the ^{13}C-labeled sodium salt (0.28 g, 0.9 mmol, 90%) as a white solid. This salt was used to generate the *o*-tolyl[α-^{13}C]diazomethane without further purification.

***o*-Tolyl[α-^{13}C]diazomethane.**[29] [*carbaldehyde*-^{13}C-*o*-tolualdehyde tosylhydrazone sodium salt (110 mg, 0.35 mmol) decomposed in the apparatus shown in Figure 2 to give the deep-red *o*-tolyl[α-^{13}C]diazomethane collected in trap I. The temperature of furnace I of Figure 2 was 100 °C, and the vacuum was at 0.1 torr.

Thermolysis of *o*-Tolyl[α-^{13}C]diazomethane.[29] Following the preparation of the *o*-tolyl[α-^{13}C]diazomethane, sublimation of the deep-red diazomethane through the hot zone (930 °C) of furnace II by removing the liquid nitrogen bath around trap I gave products (26 mg). GLC and GC/MS studies showed styrene (98%), *o*-xylene (1%), and benzene (1%). The ^{13}C NMR ($CDCl_3$) spectrum of the final products is assigned[11] as follows: 136.52 (α carbon of styrene), 128.31 (meta carbon of styrene), 127.78 (para carbon of styrene), 125.82 (ortho carbon of styrene), and 113.33 (β carbon of styrene). A repeat experiment gave the same results within experimental error.

[*carboxy*-^{13}C]-*m*-Toluic Acid.[16] The procedure described for the formation [*carboxy*-^{13}C]-*o*-toluic acid gave [*carboxy*-^{13}C]-*m*-toluic acid (3.76 g, 27.4 mmol, 91%) from *m*-bromotoluene (13.13 g, 76.8 mmol), magnesium turnings (3.68 g, 153 mmol), and 99% ^{13}C barium carbonate (5.92 g, 29.8 mmol): mp 110–112 °C; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 7.15–7.40 (m, 2 H), 7.45–7.65 (m, 2 H), 11.85 (br s, 1 H); mass spectrum (16 eV), *m/e* (relative intensity) 138 (6), 137 (100, M^+), 120 (12), M^+ calcd 137.0558, obsd 137.0556.

Methyl[α-^{13}C]benzyl Alcohol. Reduction of [*carboxy*-^{13}C]-*m*-toluic acid (0.64 g, 4.7 mmol) as described for the synthesis of *o*-methyl[α-^{13}C]benzyl alcohol gave *m*-methyl[α-^{13}C]benzyl alcohol (0.55 g, 4.5 mmol, 96%): bp 110–115 °C/30 torr; ^1H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 3.39 (br s, 1 H), 4.51 (d, 2 H, $J_{^{12}C-H\alpha}$ = 142 Hz), 6.93–7.43 (m, 4 H).

[*carbaldehyde*-^{13}C]-*m*-Toluladehyde.[26] The procedure described for the formation of [*carbaldehyde*-^{13}C]-*o*-tolualdehyde gave [*carbaldehyde*-^{13}C]-*m*-tolualdehyde (0.53 g, 4.4 mmol, 98%) from *m*-methyl[α-^{13}C]benzyl alcohol (0.55 g, 4.5 mmol): bp 95–98 °C/30 torr; ^1H NMR ($CDCl_3$) δ 2.49 (s, 3 H), 7.33–8.00 (m, 4 H), 10.15 (4, 1 H, $J_{^{13}C-H}$ = 177 Hz).

[*carbaldehyde*-^{13}C]-*m*-Toluladehyde Tosylhydrazone. Reaction of [*carbaldehyde*-^{13}C]-*m*-tolualdehyde (0.53 g, 4.4 mmol) with *p*-toluenesulfonylhydrazide as described for the formation of [*carbaldehyde*-^{13}C]-*o*-tolualdehyde tosylhydrazone gave the ^{13}C-labeled tosylhydrazone (1.05 g, 3.6 mmol, 83%): mp 118–119 °C [unlabeled, lit.[30] mp 119–119.5 °C]; ^1H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 2.42 (s, 3 H), 7.19–7.55 (m, 6 H), 7.92 (d, 2 H, J_{H-H} = 8 Hz), 8.00 (d, 1 H, $J_{^{13}C-H}$ = 160 Hz), 8.35 (br s, 1 H); mass spectrum (16 eV), *m/e* (relative intensity) 290 (2), 289 (13, M^+), 156 (9), 134 (19), 133 (57), 105 (100), M^+ calcd 289.0966, obsd 289.0971; ^{13}C NMR ($CDCl_3$) δ 148.29 (^{13}C=N).

Sodium Salt of [*carbaldehyde*-^{13}C]-*m*-Tolualdehyde Tosylhydrazone. The method described for the formation of [*carbaldehyde*-^{13}C]-*o*-tolualdehyde tosylhydrazone sodium salt provided [*carbaldehyde*-^{13}C]-*m*-tolualdehyde tosylhydrazone sodium salt (0.27 g, 0.9 mmol, 90%) as a white solid.

***m*-Tolyl[α-^{13}C]diazomethane.** Decomposition of [*carbaldehyde*-^{13}C]-*m*-tolualdehyde tosylhdrazone sodium salt (0.10 g, 0.3 mmol) as described in the preparation of *o*-tolyl[α-^{13}C]diazomethane gave *m*-tolyl[α-^{13}C]diazomethane.

Thermolysis of *m*-Tolyl[α-^{13}C]diazomethane. The *m*-tolyl[α-^{13}C]diazomethane was thermolyzed by using the procedure described for *o*-tolyl[α-^{13}C]diazomethane, affording styrene (98%), *m*-xylene (1%), and benzene (1%) in 68% overall yield (from sodium salt) by GLC and GC/MS analyses. The ^{13}C NMR ($CDCl_3$) spectrum of the final products is assigned[10] as follows: δ 128.32 (meta carbon of styrene), 127.80 (para carbon of styrene), and 125.84 (ortho carbon of styrene). A repeat experiment gave similar results within experimental error.

[*carboxy*-^{13}C]-*p*-Toluic Acid.[16] The procedure described for [*carboxy*-^{13}C]-*o*-toluic acid gave [*carboxy*-^{13}C]-*p*-toluic acid (3.90 g, 28.5 mmol, 95%) from *p*-bromotoluene (13.13 g, 76.8 mmol), magnesium turnings (3.68 g, 153 mmol), and 99% ^{13}C barium carbonate (5.92 g, 29.8 mmol): mp 180–182 °C [unlabeled, lit.[32] mp 180–181 °C]; ^1H NMR ($CDCl_3$) δ 2.43 (s, 3 H), 7.10–7.40 (m, 2 H), 8.05–8.25 (m, 2 H), 11.80 (br s, 1 H); mass spectrum (16 eV), *m/e* (relative intensity) 138 (7), 137 (100, M^+), 120 (34), M^+ calcd 137.0558, obsd 137.0559.

***p*-Methyl[α-^{13}C]benzyl Alcohol.** Reduction of [*carboxy*-^{13}C]-*p*-toluic acid (1.00 g, 7.3 mmol) as described for [*carboxy*-^{13}C]-*o*-toluic acid gave *p*-methyl[α-^{13}C]benzyl alcohol (0.88 g, 7.2 mmol, 98%): bp 113–116 °C/30 torr; ^1H NMR ($CDCl_3$) δ 2.29 (s, 3 H), 3.51 (br s, 1 H), 4.52 (d, 2 H, $J_{^{13}C-H\alpha}$ = 145 Hz), 7.06–7.40 (m, 4 H).

[*carbaldehyde*-^{13}C]-*p*-Tolualdehyde.[26] The procedure described for the formation of [*carbaldehyde*-^{13}C]-*o*-tolualdehyde gave [*carbaldehyde*-^{13}C]-*p*-tolualdehyde (0.82 g, 6.8 mmol, 95%) from *p*-methyl[α-^{13}C]benzyl alcohol: bp 103–105 °C/30 torr; ^1H NMR ($CDCl_3$) δ 2.43 (s, 3 H), 7.23–7.60 (m, 2 H), 7.70–8.23 (m, 2 H), 10.09 (d, 1 H, $J_{^{13}C-H\alpha}$ = 179 Hz).

[*carbaldehyde*-^{13}C]-*p*-Tolualdehyde Tosylhydrazone. The reaction of [*carbaldehyde*-^{13}C]-*p*-tolualdehyde (0.82 g, 6.8 mmol) with *p*-toluenesulfonohydrazide as described for the formation of [*carbaldehyde*-^{13}C-*o*-tolualdehyde tosylhydrazone gave the ^{13}C-labeled tosylhydrazone (1.60 g, 5.5 mmol, 81%): mp 150–152 °C [unlabeled, lit.[30] mp 149–151.5 °C]; ^1H NMR ($CDCl_3$) δ 2.34 (s, 3 H), 2.39 (s, 3 H), 7.19–7.45 (m, 6 H), 7.73 (d, 1 H, $J_{^{13}C-H}$ = 159 Hz), 7.87 (d, 2 H, J_{H-H} = 8 Hz), 8.15 (br s, 1 H); mass spectrum (16 eV), *m/e* (relative intensity) 290 (2), 289 (14, M^+), 156, 134 (20), 133 (58), 105 (100), M^+ calcd 289.0966, obsd 289.0968; ^{13}C NMR ($CDCl_3$) δ 148.27 (^{13}C=N).

Sodium Salt of [*carbaldehyde*-^{13}C]-*p*-Tolualdehyde Tosylhydrazone. Reaction of [*carbaldehyde*-^{13}C]-*p*-tolualdehyde tosylhydrazone (0.22 g, 0.8 mmol) with sodium hydride as described for the formation of [*carbaldehyde*-^{13}C]-*o*-tolualdehyde tosylhydrazone sodium salt gave the ^{13}C-labeled sodium salt (0.23 g, 0.7 mmol, 88%) as a white solid.

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p-Tolyl[α-^{13}C]diazomethane. Decomposition of [*carbaldehyde*-^{13}C]-*p*-tolualdehyde tosylhydrazone sodium salt gave *p*-tolyl[α-^{13}C]diazomethane (0.1 g, 0.3 mmol) as described in the formation of *o*-tolyl[α-^{13}C]diazomethane.

Thermolysis of p-Tolyl[α-^{13}C]diazomethane. Thermolysis of *p*-tolyl[α-^{13}C]diazomethane as described for *o*-tolyl[α-^{13}C]diazomethane gave styrene (98%), *p*-xylene (1%), and benzene (1%) in 79% overall yield by GLC and GC/MS analyses. The ^{13}C NMR ($CDCl_3$) spectrum of the final product is assigned[10] as follows: 128.31 (meta carbon of styrene) and 127.79 (para carbon of styrene). A repeat experiment gave similar results within experimental error.

Thermolysis of [2.2]Paracyclophane. Thermolysis of [2.2]paracyclophane (61 mg, 0.29 mmol) under the same conditions used for the thermolysis of [α-^{13}C]benzocyclobutene afforded 33 mg products. GLC and GC/MS analyses showed styrene (55%), *p*-xylene (31%), benzene (4%), benzocyclobutene (4%), and toluene (3%).

Thermolysis of [2.2]Metacyclophane. Thermolysis of [2.2]metacyclophane[32] (57 mg, 0.27 mmol) under the same conditions used for the thermolysis of [α-^{13}C]benzocyclobutene afforded 32 mg products. GLC and GC/MS analyses showed styrene (18%), *p*-xylene (35%), *m*-xylene (3%), benzocyclobutene (1%), benzene (7%), and toluene (22%).

Thermolysis of [2.2]Metaparacyclophane. Thermolysis of [2.2]metaparacyclophane[33] (28 mg, 0.13 mmol) under the same conditions used for the thermolysis of [α-^{13}C]benzocyclobutene gave 17 mg of products. GLC and GC/MS analyses showed styrene (10%), *p*-xylene (63%), *m*-xylene (1%), benzocyclobutene (1%), benzene (3%), and toluene (15%).

***p*-Ethyl[*carboxy*-^{13}C]benzoic Acid.** The procedure described for the synthesis of [*carboxy*-^{13}C]-*o*-toluic acid gave *p*-ethyl[*carboxy*-^{13}C]benzoic acid (6.74 g, 44.6 mmol, 89%) from *p*-bromoethylbenzene (18.51 g, 100 mmol), magnesium turnings (6.15 g, 256 mmol), and 99% ^{13}C barium carbonate (9.87 g, 50.0 mmol): bp 111.5-113 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (t, 3 H, J_{H-H} = 7 Hz), 2.73 (q, 2 H, J_{H-H} = 7 Hz), 7.29 (d, 2 H, J_{H-H} = 8 Hz), 8.04 (dd, 2 H, J_{H-H} = 8, $J_{^{13}C-H}$ = 4 Hz), 12.30 (br s, 1 H); mass spectrum (70 eV), *m/e* (relative intensity) 152 (4), 151 (44, M^+), 136 (45), 135 (2), 107 (26), 106 (14), 105 (100), 91 (25), M^+ calcd 151.0715, obsd 151.0719; ^{13}C NMR ($CDCl_3$) δ 172.45 (^{13}COOH).

***p*-Ethyl[α-^{13}C]benzyl Alcohol.** Reduction of *p*-ethyl[*carboxy*-^{13}C]-benzoic acid (1.34 g, 8.9 mmol) as described for the reduction of [*carboxy*-^{13}C]-*o*-toluic acid gave *p*-ethyl[α-^{13}C]benzyl alcohol (1.21 g, 8.8 mmol, 99%) as a colorless liquid: bp 144-146 °C/30 torr; ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 3 H, J_{H-H} = 7 Hz), 1.82 (br s, 1 H), 2.66 (q, 2 H, J_{H-H} = 7 Hz), 4.65 (d, 2 H, $J_{^{13}C-H\alpha}$ = 144 Hz), 7.19-7.50 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 65.08 ($^{13}CH_2OH$).

***p*-Ethyl[α-^{13}C]benzyl Chloride.** Reaction of *p*-ethyl[α-^{13}C]benzyl alcohol (1.21 g, 8.8 mmol) with concentrated hydrochloric acid as described in the formation of *o*-methyl[α-^{13}C]benzyl chloride gave *p*-ethyl[α-^{13}C]benzyl chloride (1.33 g, 8.5 mmol, 97%): bp 105-107 °C/30 torr; ^{1}H NMR ($CDCl_3$) δ 1.30 (t, 3 H, J_{H-H} = 7 Hz), 2.71 (q, 2 H, J_{H-H} = 7 Hz), 4.62 (d, 2 H, $J_{^{13}C-H\alpha}$ = 152 Hz), 7.10-7.50 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 46.23 ($^{13}CH_2Cl$).

***p*-Ethyl[α-^{13}C]toluene.** Dropwise addition of *p*-ethyl[α-^{13}C]benzyl chloride (1.35 g, 8.7 mmol) in 87 mL of dimethyl sulfoxide to a well-stirred solution of sodium borohydride (1.64 g, 44 mmol) in 87 mL of dimethyl sulfoxide gave a clear solution. Stirring (6 h) at room temperature, dilution with distilled water (100 mL), extraction with ether, drying (Na_2SO_4), filtration, concentration under reduced pressure, and distillation gave *p*-ethyl[α-^{13}C]toluene (0.84 g, 6.9 mmol, 80%) as a colorless liquid: bp 160-163 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (t, 3 H, J_{H-H} = 7 Hz), 2.74 (q, 2 H, J_{H-H} = 7 Hz), 2.45 (d, 3 H, $J_{^{13}C-H\alpha}$ = 126 Hz), 7.10-7.40 (m, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 122 (3), 121 (26, M^+), 106 (100), 105 (23), 92 (14), 91 (2), M^+ calcd 121.0973, obsd 121.0980; ^{13}C NMR ($CDCl_3$) δ 20.93 ($Ar^{13}CH_3$).

Thermolysis of p-Ethyl[α-^{13}C]toluene. Neat *p*-ethyl[α-^{13}C]toluene (121 mg, 1.00 mmol), thermolyzed under exactly the same conditions as the pyrolysis of [α-^{13}C]benzocyclobutene, gave 93 mg of products. GLC and GC/MS showed styrene (5.7%), benzene (0.8%), toluene (6.7%), ethylbenzene (5.1%), *p*-xylene (16.2%), starting material (34.5%), *p*-methylstyrene (26.5%), indene (0.3%), phenylacetylene (0.5%), benzocyclobutene (0.3%), and 1-methylene-4,4-dimethylcyclohexadiene (0.3%). The ^{13}C NMR ($CDCl_3$) spectrum of the final products is assigned[10] as follows: δ 136.54 (α carbon of styrene), 128.31 (meta carbon of styrene), 127.79 (para carbon of styrene), 125.82 (ortho carbon of styrene), 113.34 (β carbon of styrene), 128.30 (benzene), 21.36 (methyl carbon of toluene), 15.52 (β carbon of ethylbenzene), 28.84 (α carbon of ethylbenzene), 21.03 (methyl carbon of *p*-xylene), 20.93 (aromatic methyl carbon of *p*-ethyltoluene), 28.46 ($^{13}CH_2CH_3$ of *p*-ethyltoluene), 15.73 ($CH_2{}^{13}CH_3$ of *p*-ethyltoluene), 21.15 (methyl carbon of *p*-methylstyrene), 136.75 (α carbon of *p*-methylstyrene), and 112.70 (β carbon of *p*-methylstyrene). A repeat experiment gave similar results within experimental error.

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A Theoretical Study of Proton Transfer in Lithium Carbonyl and Lithium Enolate Complexes

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Abstract: MNDO and ab initio (3-21+G) calculations have been used to study the mechanism of deprotonation of acetaldehyde by lithium amide to form the lithium enolate amine complex. The transition structure, which is characterized by a nearly colinear C-H-N arrangement involving the transferring proton, is predicted to be very reactant-like, suggesting that the cis to trans ratio can be predicted from differences in the conformational energy in the carbonyl compounds. The reverse reaction, the intramolecular protonation of the enolate to reform acetaldehyde, is predicted to be endothermic by 30.2 kcal/mol (3-21+G). However, the reaction of the enol with the lithium-amine complex is predicted to be exothermic by 16.3 kcal/mol. The observed *intramolecular* proton transfer in acid solution can be rationalized by solvent (H_2O) deprotonation of oxygen concurrent with protonation of nitrogen as the concerted proton transfer proceeds.

The stereoselectivity of enolate formation from carbonyl compounds using lithium compounds has received much attention.[1-17] The ratio of geometric isomers can be altered by changing the countercation,[5] the solvent,[15] and the size of the substituents on

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