

observed. Irradiation (>284 nm) of **9** gave benzocyclobutene (**10**). Irradiation (>261 nm) of 1-methylcyclohepta-1,2,4,6-tetraene (**8**) gave styrene (**11**). The intermediate carbene **5** was generated by irradiation of diazocompound **1d**. The conversion of **5** to styrene (**11**) could be accomplished by irradiation or by warming to 80 K using a xenon matrix in place of argon.¹⁴ No evidence for photochemical conversion of styrene to carbene **5** or to other products in the series was observed. Flash vacuum thermolysis (375 °C) of diazo compounds **1a** and **1b** followed by trapping of the pyrolysate by cocondensation with argon at 28 K gave styrene (**11**) and benzocyclobutene (**10**) (ratio ca. 1:0.8) as characterized by infrared spectroscopy. In addition, small amounts of both 4- and 5-methylcyclohepta-1,2,4,6-tetraenes were observed in the infrared spectrum. Thermolysis of **1c** gave styrene (**11**) and benzocyclobutene (**10**) (ratio ca. 0.75:1), with no detectable cycloheptatetraenes. Thermolysis of **1d** gave styrene cleanly.

The observations described above lead to the mechanism shown in Scheme I. This mechanism is consistent with the labeling experiments described in the literature^{3,4} and with labeling experiments described in the accompanying communications.^{15,16} Labeling results¹⁵ require the conversions **4** → **7**, **7** → **3**, and **6** → **2** in addition to the reverse conversions required by the present investigation. Equilibration of phenylmethylene and cyclohepta-1,2,4,6-tetraene⁵ and of phenylnitrene and 1-azacyclohepta-1,2,4,6-tetraene¹⁷ are documented and support such interconversions. The mechanism in Scheme I accounts for all observations in the rearrangements of the tolyldiazomethanes. Each step can occur thermally or photochemically. Mechanisms proposed previously for these arrangements have invoked bicyclo[4.1.0]hepta-2,4,6-triene intermediates.^{1,2a,b,3,4} We have not observed such intermediates in the tolylmethylene rearrangements or in the phenylmethylene-cycloheptatetraene system.⁵ The absence of bicyclo[4.1.0]hepta-2,4,6-triene intermediates is not due to our inability to detect or observe such species. The benzobicyclo[4.1.0]hepta-2,4,6-trienes are readily observed in the irradiation of the matrix-isolated naphthyldiazomethanes.¹⁸ We conclude that bicyclo[4.1.0]hepta-2,4,6-trienes are not required intermediates in the rearrangements of the tolylmethylenes, but they may be part of more complex equilibria at high temperature.^{4c} The details of the arylmethylene-cycloheptatetraene interconversion are considered in a separate publication.¹⁹ Finally, it should be pointed out that the mechanism presented in Scheme I suggests a novel mechanism for the thermal conversion of benzocyclobutene to styrene reported by Baron and DeCamp.^{15,16,20}

Acknowledgment. This research was supported by Grant CHE81-11196 from the National Science Foundation and by a National Science Foundation Predoctoral Fellowship (R.J.M.). We are grateful to Professor W. S. Trahanovsky for a preprint of his manuscript.

Registry No. **1a**, 23304-24-7; **1b**, 40154-67-4; **1c**, 698-20-4; **1d**, 22293-10-3; **2**, 4190-16-3; **3**, 40148-85-4; **4**, 35745-45-0; **5**, 6393-09-5; **6**, 93001-01-5; **7**, 93001-00-4; **8**, 93000-99-8; **9**, 32796-95-5; **10**, 4026-23-7; **11**, 100-42-5.

Supplementary Material Available: A tabulation of the infrared absorptions of carbenes **2**, **3**, and **5** and methylcycloheptatetraenes **6** and **7** (1 page). Ordering information is given on any current masthead page.

(14) McMahan, R. J.; Chapman, O. L. *J. Am. Chem. Soc.*, submitted for publication.

(15) Chapman, O. L.; Tsou, U. E. *J. Am. Chem. Soc.*, following paper in this issue.

(16) Trahanovsky, W. S.; Scribner, M. E. *J. Am. Chem. Soc.*, second following paper in this issue.

(17) Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 6245-6247. Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 334-337.

(18) West, P. R. Ph.D. Dissertation, UCLA, Los Angeles, CA, 1981.

(19) Chapman, O. L.; McMahan, R. J.; West, P. R., manuscript in preparation.

(20) Baron, W. J.; DeCamp, M. R. *Tetrahedron Lett.* **1973**, 4225-4228.

Mechanism of the Thermal Isomerization of Benzocyclobutene[†] to Styrene¹

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Received April 9, 1984

The thermal rearrangement of benzocyclobutene to styrene² poses an intriguing problem in mechanism. The simplest mechanism that can be written (Scheme I) breaks a bond adjacent to the aromatic ring with subsequent hydrogen transfer giving styrene. Photochemical experiments on the tolylmethylenes matrix isolated in argon suggest Scheme II for the isomerization of benzocyclobutene to styrene.³ This mechanism has a direct path from *o*-tolylmethylene to styrene and an alternate path in which the methyl group migrates completely around the ring. The branching point for the two paths is *o*-tolylmethylene (**1**). Schemes I and II can be distinguished by labeling the methylene group of benzocyclobutene with ¹³C or by deuterium-labeling experiments.⁴ Scheme II³ also explains the rearrangement of the tolyldiazomethane to benzocyclobutene and styrene.⁵ Several mechanisms⁶ have been considered for this process.

Thermolysis (930 °C (0.1 torr))⁷ of methylene-labeled benzocyclobutene (99% ¹³C)⁸ gave a total crude product¹¹ with the ¹³C NMR spectrum shown in Figure 1. Only labeled products are observed in this spectrum.¹² It is clear that the major labels (corrected for relative sensitivity)¹³ are in the β- (48 ± 2%) and

[†]The title compound is correctly named 1,2-dihydrobenzocyclobutene. Benzocyclobutene is the systematic name for a compound with four double bonds.

(1) Chapman, O.; Tsou, U. "Abstracts of Papers", 186th Meeting of the American Chemical Society, Washington, DC, Aug 1983; American Chemical Society: Washington, DC, 1983; ORGN 56.

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

(3) Chapman, O. L.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.*, preceding paper in this issue.

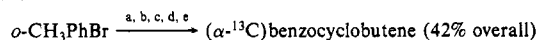
(4) Manuscript of a paper presented at the 186th ACS Meeting, Washington, DC: Trahanovsky, W. S.; Scribner, M. E. *J. Am. Chem. Soc.*, following paper in this issue.

(5) (a) Vander Stouw, G. G. Ph.D. Dissertation, The Ohio State University, Columbus, OH 1964. (b) Baron, W.; Jones, M., Jr.; Gaspar, P. *J. Am. Chem. Soc.* **1970**, *92*, 4739-4740.

(6) (a) Jones, W. M. In "Rearrangement in Ground and Excited States"; deMayo, P. Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 3. (b) Wentrup, C. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, Chapter 4. (c) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173-251. (d) Wentrup, C. "Reactive Molecules"; Wiley: New York, 1984; Chapter 4.

(7) The compound was passed through a 1/2-in. diameter quartz tube packed with quartz chips at 930 °C and 0.1 torr. The tube was placed in an E. H. Sargent and Co. 49090 tube furnace with a 17-in. hot zone. The products were trapped in a cold trap at 77 K.

(8) (a)



a, Mg; b, ¹³CO₂ (99% ¹³C); c, LiAlH₄; d, HCl; e, flash-vacuum pyrolysis (750 °C (0.1 torr)).³ (b) (α-¹³C)Benzocyclobutene: bp 141-143 °C (unlabeled lit.^{10a} 143 °C); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ 29.71 (methylene carbon^{10b}); 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.

(9) Morella, M. J.; Trahanovsky, W. S. *Tetrahedron Lett.* **1979**, 4435-4436.

(10) (a) Sanders, A.; Giering, W. P. *J. Org. Chem.* **1973**, *38*, 3055. (b) Motell, E. L.; Lauer, D.; Maciel, G. D. *J. Phys. Chem.* **1973**, *77*, 1865-1868.

(11) GLC and GC-MS studies show that the product distribution is as follows: styrene, 95.5%; starting material, 2.0%; *o*-xylene, 1.4%; *p*-xylene, 0.5%. The total mass recovery was 71%.

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

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

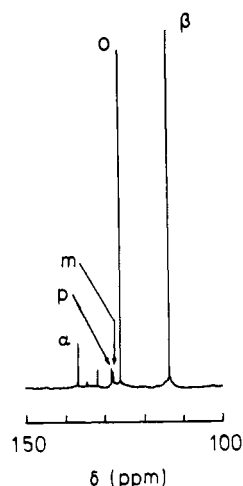
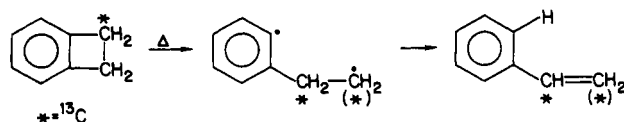
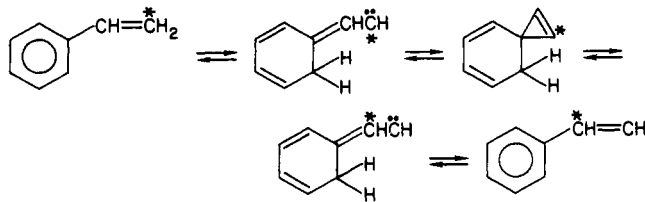


Figure 1. ^{13}C NMR spectrum of crude product from thermolysis of methylene-labeled benzocyclobutene (99% ^{13}C). Only labeled positions are visible. Labeled styrene positions¹⁵ are β (113.34), ortho (125.82), α (136.54), meta (128.31), and para (127.79). The origin of the peak at 131.92 is not known. Traces of ^{13}C -methyl-labeled *o*- and *p*-xylene¹¹ are observed at higher field.

Scheme I

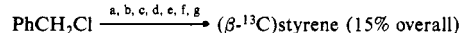


o-positions ($30 \pm 2\%$) with smaller amounts in the α - ($14 \pm 2\%$), *p*- ($4 \pm 2\%$), and *m*-positions ($4 \pm 2\%$). No double-labeled products are observed, and no label is lost. Intermolecular carbon transfers are thus unlikely. Scheme II is consistent with the major labels (β , o) observed. The presence of an α -labeled styrene is consistent with Scheme I as a minor path, but subsequent studies have shown that the α label can be derived from β -labeled styrene. Thermolysis (930°C)⁷ of (β - ^{13}C)styrene (99%)¹⁴ gave α -labeled styrene (δ 136.54)¹⁵ in 4% yield. A possible mechanism¹⁶ for this



process involves hydrogen transfer from the β -carbon to an ortho position, followed by cyclization of the carbene, ring opening in the opposite sense, and hydrogen transfer back to the β -carbon. The β label (48%) is equal to the sum of the other labels (ortho + α + meta + para = 52%) within experimental error. It thus seems likely that ortho label is the source of the minor labels. Scheme I gives α and β label equally, reducing ortho label without effect on β label. We estimate that approximately 25% of the styrene is produced by Scheme I.

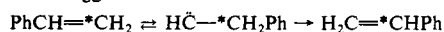
(14) (a)



a, Mg; b, $^{13}\text{CO}_2$ (99% ^{13}C); c, LiAlH_4 ; d, Na; e, CS_2 ; f, CH_3I ; g, xanthate pyrolysis (210°C), distillation. (b) (β - ^{13}C)styrene: bp $145\text{--}147^\circ\text{C}$; ^1H NMR (CDCl_3) δ 5.28 (dd, 1 H, $J = 160, 12$ Hz), 5.74 (dd, 1 H, $J = 160, 18$ Hz), 6.71 (dd, 1 H, $J = 18, 12$ Hz), 7.05–7.50 (m, 5 H); ^{13}C NMR (CDCl_3) δ 113.34 (β carbon¹⁵).

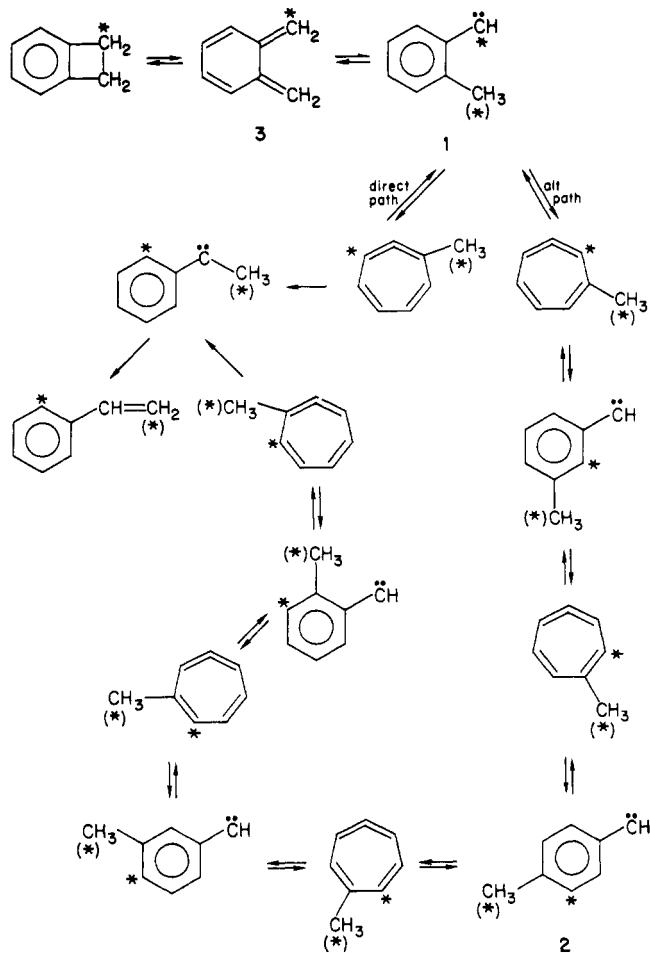
(15) (a) ^{13}C NMR spectrum from Sadtler Research Laboratories, Inc., Compound 4006C. (b) Stothers, J. B.; Dhimi, K. S. *Can. J. Chem.* **1965**, *43*, 510–520.

(16) A referee suggested an alternative mechanism.

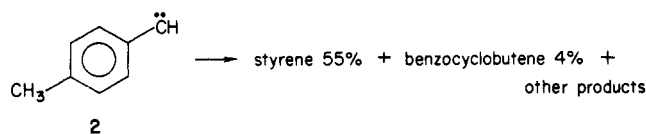
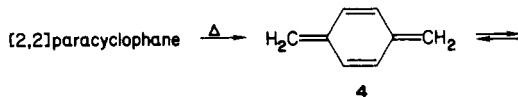


We have no evidence against such a possibility.

Scheme II



The interconversion of *o*-xylene (3) and *o*-tolymethylene (1) suggested the possibility that *p*-xylene (4) might undergo an analogous equilibration with *p*-tolymethylene (2). Thermolysis



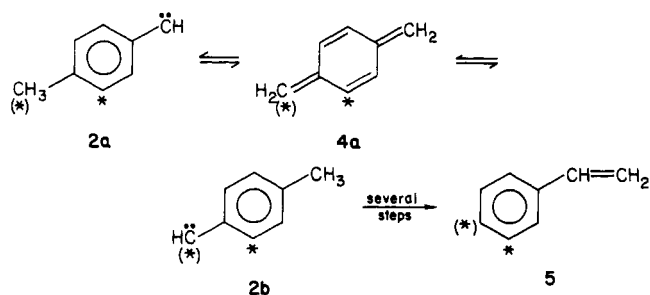
(930°C)⁷ of [2.2]paracyclophane, a precursor of *p*-xylene,¹⁷ gave styrene (55%), *p*-xylene (31%), benzene (4%), toluene (3%), and benzocyclobutene (4%). The total mass recovery was 54%. Formation of styrene and benzocyclobutene is consistent with equilibration of 4 and 2 and further reaction of 2 by Scheme II.

The origins of the minor meta and para labels are also of interest. In the alternate path of Scheme II, *p*-tolymethylene (2) is formed. Equilibration of labeled 2a with the corresponding *p*-xylene (4a) gives 2b which via Scheme II produces meta- and para-labeled styrenes (5). This minor mechanism was not detected in the deuterium-labeling study of Trahanovsky and Scribner.⁴ It does not occur at lower temperatures as shown by ^{13}C -labeling studies¹⁸ and deuterium-labeling studies¹⁹ starting with the tolyldiazomethanes. Trahanovsky and Morella⁹ have

(17) (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.

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

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



shown that generation of *o*-xylylene below 750 °C gives benzocyclobutene. Higher temperatures are required for the *o*-xylylene to *o*-tolylmethylene interconversion.

The present study and the matrix investigation of the tolylmethylenes and methylcycloheptatetraenes³ reveal a mechanism that operates over a 1200-deg range.

Acknowledgment. This research was supported by Mobil Corp. We are indebted to Professor W. S. Trahanovsky for a preprint of his manuscript.

Registry No. *o*-CH₃PhBr, 95-46-5; Mg, 7439-95-4; ¹³CO₂, 1111-72-4; LiAlH₄, 16853-85-3; HCl, 7647-01-0; benzocyclobutane, 694-87-1; styrene, 100-42-5; [2.2]paracyclophane, 1633-22-3; (*α*-¹³C)benzocyclobutane, 93000-71-6.

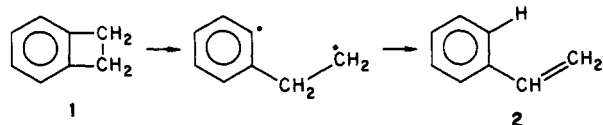
Methyl-Group and Deuterium-Atom Labeling in the Mechanism of the Rearrangement of Benzocyclobutene[†] to Styrene¹

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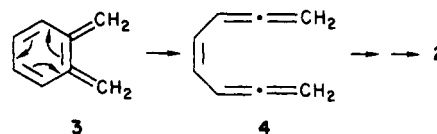
Received April 10, 1984

The pyrolysis of benzocyclobutene (1) gives styrene (2) in high yield.² This rearrangement involves only the cleavage of a carbon-carbon bond and the shift of a hydrogen atom, but the simple mechanism consisting of homolytic cleavage of the C-C bond followed by a 1,3-shift of a hydrogen atom is questionable because the first step is not clearly a favorable reaction. Moreover,

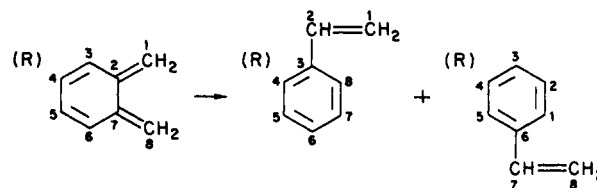


it is well established that the electrocyclic opening of 1 to *o*-quinodimethane (3) is a favorable reaction,³ and mechanisms can be written that transform 3 into 2. In an attempt to define the mechanism of the rearrangement of 1 to 2, we have studied the pyrolysis of methyl-group and deuterium-atom labeled benzocyclobutenes, and the results of this study are reported herein.

Mechanisms can be written which convert 3 to 2 by a series of 1,2-carbon and 1,2-hydrogen shifts or by a sequence involving bisallene 4⁴ as an intermediate. These mechanisms have the

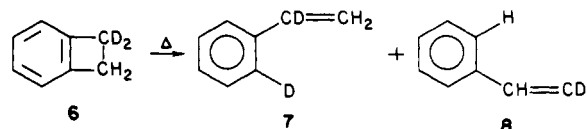


fundamental feature of keeping intact the linear chain of eight carbon atoms of 3, and therefore a 4-substituted benzocyclobutene should give the *ortho*- and *meta*-substituted styrenes. Thus, our



observation that the pyrolysis (900 °C) of 4-methylbenzocyclobutene (5)⁵ gives only the *m*- and *p*-methylstyrenes (70%, *meta/para* = 1.2) clearly rules out these mechanisms.

The simple two-step mechanism is consistent with the production of *m*- and *p*-methylstyrenes from 5 but is not consistent with the results we obtained from the pyrolysis (800 °C) of *α*,*α*-dideuteriobenzocyclobutene (6).⁶ By this mechanism, 6 should give only *d*₂ styrenes 7 and 8 and this was not observed. Both



¹H and ²H NMR analysis showed extensive scrambling among the three vinyl positions and an *ortho* position.⁷

Professor Chapman and his co-workers have observed that the pyrolysis of *α*-¹³C labeled 1 gives 2 with most of the label in the *β* and *ortho* positions.⁸ These results also rule out the simple two-step mechanism but are consistent with a mechanism involving arylcarbene-cycloheptatetraene interconversions.⁹ According to this mechanism, the pyrolysis of 6 should give six *d*₂ styrenes (Scheme I). The NMR analysis of the styrenes obtained from 6 was consistent with the production of all six species, but further evidence for the deuterium scrambling was obtained as follows. The deuterated styrenes were converted to deuterated *α*-phenethanols,¹⁰ and analysis by mass spectroscopy showed that ca. 100% of the *α*-phenethanol contained two deuteriums and that the major cationic fragment, the *α*-hydroxybenzyl cation, was 48% *d*₀, 46% *d*₁, and 6.5% *d*₂. This cationic fragment is produced by loss of a methyl group at a rate faster than deuterium scrambling,¹¹ and therefore the deuterium content of this fragment provides a measure of the deuterium content of the terminal methylene group of the deuterated styrenes. Thus, the deuterated styrenes consisted of 6.5% 7, 46% 9-12, and 48% 8.

According to the mechanism shown in Scheme I, each deuterated styrene should be produced in 16.7% yield if there are no kinetic isotope effects. Therefore, the low yield of 7, formed by two deuterium shifts, and the high yield of 8, formed by two

(5) Garrett, J. M. *Tetrahedron Lett.* 1969, 191-194.

(6) Morello, M. J.; Trahanovsky, W. S. *Tetrahedron Lett.* 1979, 4435-4436.

(7) The pyrolyzate was analyzed by comparing the 300-MHz ¹H and ²H NMR spectra of the pyrolyzate to the spectra of specifically deuterated styrenes.

(8) Chapman, O. L.; Tsou, U. E.; McMahon, R. J.; West, P. R., personal communication. See preceding two papers in this issue.

(9) (a) Jones, W. M. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 3. (b) Wentrup, C. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, Chapter 4. (c) Wentrup, C. *Adv. Heterocycl. Chem.* 1981, 28, 231-361.

(10) The deuterated styrenes were converted to the *α*-phenethanols by epoxidation followed by lithium aluminum hydride reduction of the epoxides.

(11) Nibbering, N. M. M.; DeBoer, Th. *Org. Mass Spectrom.* 1968, 1, 365-390.

[†] The title compound is correctly named 1,2-dihydrobenzocyclobutene. Benzocyclobutene is the systematic name for a compound with four double bonds.

(1) Trahanovsky, W.; Scribner, M. "Abstracts of Papers", 186th Meeting of the American Chemical Society, Washington, DC, Aug 1983; American Chemical Society: Washington, DC, 1983; ORGN 57.

(2) (a) Baron, W. J.; DeCamp, M. R. *Tetrahedron Lett.* 1973, 4225-4228. (b) Berman, M. R.; Comita, P. B.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* 1980, 102, 5692-5694. (c) Swenson, K. E.; Trahanovsky, W. S. *J. Org. Chem.* 1981, 46, 2984-2985.

(3) (a) McCullough, J. J. *Acc. Chem. Res.* 1980, 13, 270-276 and references cited therein. (b) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* 1980, 41-61.

(4) Evidence for the reverse reaction, 4 to 3, has been reported: Ben-Efraim, D. A.; Sondheimer, F. *Tetrahedron Lett.* 1963, 313-315.