formation of $H_2O^{-}\cdot$ can be bracketed between -50 and -18 kJ/mol. The present results do not provide information about bond lengths and bond angles in the $H_2O^{-}\cdot$ species. Apparently being trapped in a local energy minimum its geometry may differ substantially from that of ground-state water, which stabilizes the $H_2O^{-}\cdot$ ion with respect to electron detachment as indicated by theoretical calculations.[9,10]

Finally, it should be noted that at ambient temperature an optimum yield of $H_2O^{-}\cdot$ could be obtained. The production of $H_2O^{-}\cdot$ decreased as the cell was slightly heated up by the filament.

Nevertheless, the generation of $H_2O^{-}\cdot$ could be reproduced over a period of 6 months, so that we are forced to assume that this ion can exist as a stable species in the gas phase.

Acknowledgment. We thank F. A. Pinkse for his expert technical assistance and the Netherlands Organization for Pure Research (SON/ZWO) for financial support.

Registry No. $H_2O^{-}\cdot$, 12259-30-2; $O^{-}\cdot$, 14337-01-0; CH_3NH_2, 74-89-5; $C_2H_5NH_2$, 75-04-7; $(CH_3)_2NH$, 124-40-3; CH_2O, 50-00-0; $CH_3NH\cdot$, 15622-51-2; $C_2H_5NH\cdot$, 41084-92-8; $(CH_3)_2N\cdot$, 15337-44-7.

---

[22] $\Delta H_f°(CH_2NH)$ = 94 kJ/mol, as calculated on the basis of group additivity rules: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

Rearrangements of Tolylmethylenes via Cycloheptatetraenes: Formation of Benzocyclobutene and Styrene†

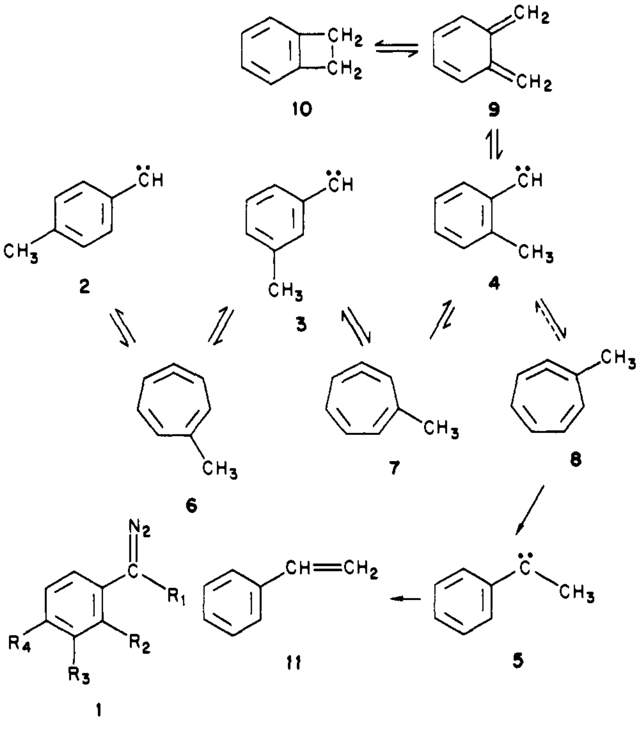
Orville L. Chapman,* Robert J. McMahon, and
Paul R. West

Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, California 90024

Received April 9, 1984

The thermolysis of *o*-, *m*-, and *p*-tolyldiazomethanes to styrene and benzocyclobutene poses a mechanism problem of substantial interest. Several intriguing solutions to this problem have been suggested,[1-4] and labeling studies,[1,3,4] have placed severe mechanistic constraints on possible solutions. Our studies on the phenylmethylene–cycloheptatetraene interconversion[5] prompted an investigation of the tolylmethylene rearrangement. We now wish to propose a mechanism for the rearrangement of the tolylmethylenes via cycloheptatetraenes and for the formation of benzocyclobutene and styrene in which all intermediates are observed.

Scheme I



	R_1	R_2	R_3	R_4
a	H	H	H	CH_3
b	H	H	CH_3	H
c	H	CH_3	H	H
d	CH_3	H	H	H

Irradiation (>470 nm) of diazocompounds **1a–d** matrix isolated in argon at 10–15 K[6] provided the carbenes **2–5**. Each carbene was shown to be a triplet by electron spin resonance studies.[9] The UV/visible spectra of **2–5** showed the π–π^* transitions characteristic of triplet arylcarbenes.[10] In addition, complete infrared spectra of **2**, **3**, and **5** were obtained.[11] The methylcycloheptatetraenes (**6–8**) were observed by infrared spectroscopy and each showed the bands at ~1810 cm^{-1} characteristic of the cycloheptatetraene–allene chromophore.[5] Complete infrared spectra of **6** and **7** were obtained.[11] 5-Methylcyclohepta-1,2,4,6-tetraene (**6**) was formed as the sole primary photoproduct (>416 nm) from **2**. Both 4- and 5-methylcyclohepta-1,2,4,6-tetraenes were formed from **3**. Irradiation (>261 nm) of 5-methylcyclohepta-1,2,4,6-tetraene gave 4-methylcyclohepta-1,2,4,6-tetraene, thus establishing the interconversion of **6** and **7**. Irradiation (>470 nm) of **1c** gave predominately *o*-xylylene (**9**)[12] via hydrogen atom transfer in carbene **4**.[13] A small amount of ring-expansion product, 1-methylcyclohepta-1,2,4,6-tetraene (**8**; 790, 710 cm^{-1}) was also

---

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

[1] Vander Stouw, G. F. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1964. Vander Stouw, G. F.; Kraska, A. R.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 1655–1661.

[2] (a) Joines, R. C.; Turner, A. B.; Jones, W. M. *J. Am. Chem. Soc.* **1969**, *91*, 7754–7755. Jones, W. M.; Joines, R. C.; Myers, J. A. Mitsuhashi, T.; Krajca, K. E.; Waali, E. E.; Davis, T. L.; Turner, A. B. *J. Am. Chem. Soc.* **1973**, *95*, 826–835. (b) Baron, W. J.; Jones, M.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 4739–4740. (c) Wentrup, C.; Wilzek, K. *Helv. Chim. Acta* **1970**, *53*, 1459–1463. Gleiter, R.; Rettig, W.; Wentrup, C. *Helv. Chim. Acta* **1974**, *57*, 2111–2124.

[3] Schissel, P. O.; Kent, M. E.; McAdoo, M. J.; Hedaya, E. *J. Am. Chem. Soc.* **1970**, *92*, 2147–2149. Hedaya, E.; Kent, M. E. *J. Am. Chem. Soc.* **1971**, *93*, 3283–3285.

[4] (a) Jones, W. M.; Brinker, U. H. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, Chapter 3. (b) Jones, W. M. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 3. (c) Wentrup, C. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, Chapter 4. (d) Wentrup, C. "Reactive Molecules"; Wiley-Interscience: New York, 1984; Chapter 4.

[5] West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779–1782.

[6] Apparatus for the observation of matrix-isolated species by electron spin resonance,[8] infrared,[7] and ultraviolet[7] spectroscopy has been described previously.

[7] Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P.; Shou, H.-S., manuscript in preparation. Sheridan, R. S. Ph.D. Dissertation, UCLA, Los Angeles, CA, 1979.

[8] Kreil, C. L. Ph.D. Disseration, UCLA, Los Angeles, CA, 1983.

[9] **2**, D/hc = 0.516 cm^{-1}, E/hc = 0.0240 cm^{-1}; **3**, D/hc = 0.517 cm^{-1}, E/hc = 0.0246 cm^{-1}, rotomers indistinguishable; **4**, D/hc = 0.503 cm^{-1}, E/hc = 0.0253 cm^{-1}, rotomers indistinguishable; **5**, D/hc = 0.508 cm^{-1}, E/hc = 0.0278 cm^{-1}.

[10] Compound **2**, λ_{max} 444, 436, 429, 426, 422, 418, 415, 411, 408, 405, 402, 398, 395 nm; **3**, λ_{max} 448, 439, 433, 430, 426, 424, 420, 415, 410, 403, 399, 394 nm; **4**, λ_{max} 450, 440, 437, 435, 431, 427, 422, 419, 417, 413, 249, 244 nm; **5**, λ_{max} 449, 446, 432, 428, 417, 412, 405, 399, 392, 388, 381, 251, 244 nm. Our experimental technique does not permit the determination of extinction coefficients.

[11] A tabulation of the infrared absorptions of carbenes **2**, **3**, and **5** and methylcycloheptatetraenes **6** and **7** is available as supplementary material.

[12] Identified by comparison of the ultraviolet and infrared spectra with those of the authentic material matrix isolated in argon: Tseng, K. L.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4840–4842.

[13] Carbene **4** does not absorb light beyond 450 nm (vide supra). Therefore, formation of *o*-xylylene (**9**) must occur by a thermal reaction, even at the cryogenic temperatures employed (15 K).

0002-7863/84/1506-7973$01.50/0

J. Am. Chem. Soc. **1984**, *106*, 7974–7976

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 results[15] 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-tetraene[5] and of phenylnitrene and 1-azacyclohepta-1,2,4,6-tetraene[17] 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 bicyco[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) McMahon, 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.; McMahon, 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 Styrene[1]

Orville L. Chapman* and Uh-Po Eric Tsou

Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, California 90024

Received April 9, 1984

The thermal rearrangement of benzocyclobutene to styrene[2] 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 ^{13}C or by deuterium-labeling experiments.[4] Scheme II[3] also explains the rearrangement of the tolyldiazomethane to benzocyclobutene and styrene.[5] Several mechanisms[6] have been considered for this process.

Thermolysis (930 °C (0.1 torr))[7] of methylene-labeled benzocyclobutene (99% ^{13}C)[8] gave a total crude product[11] with the ^{13}C 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)

$$o\text{-CH}_3\text{PhBr} \xrightarrow{\text{a, b, c, d, e}} (\alpha\text{-}^{13}\text{C})\text{benzocyclobutene (42\% overall)}$$

a, Mg; b, ^{13}CO$_2$ (99% ^{13}C); c, LiAlH$_4$; d, HCl; e, flash-vacuum pyrolysis (750 °C (0.1 torr)).[9] (b) (α-^{13}C)Benzocyclobutene: bp 141–143 °C (unlabeled lit.[10a] 143 °C); ^{1}H 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); ^{13}C NMR (CDCl$_3$) 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 ^{13}C 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 ^{13}C-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.

0002-7863/84/1506-7974$01.50/0