

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; benzocyclobutene, 694-87-1; styrene, 100-42-5; [2.2]paracyclophane, 1633-22-3; (*α*-¹³C)benzocyclobutene, 93000-71-6.

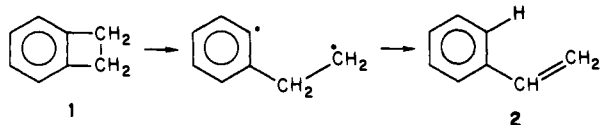
Methyl-Group and Deuterium-Atom Labeling in the Mechanism of the Rearrangement of Benzocyclobutene[†] to Styrene¹

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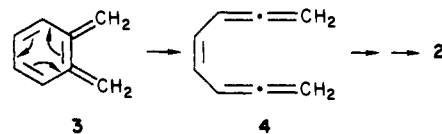
Received April 10, 1984

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,

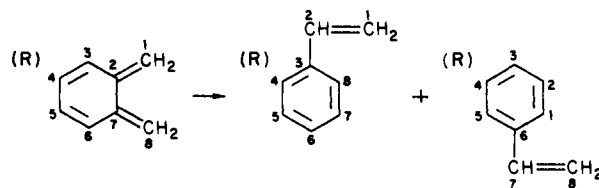


it is well established that the electrocyclic opening of 1 to *o*-quinodimethane (3) is a favorable reaction,³ and mechanisms can be written that transform 3 into 2. In an attempt to define the mechanism of the rearrangement of 1 to 2, we have studied the pyrolysis of methyl-group and deuterium-atom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

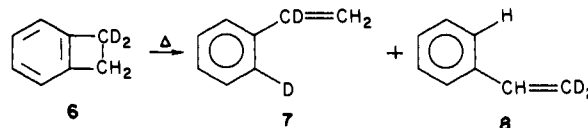


fundamental feature of keeping intact the linear chain of eight carbon atoms of 3, and therefore a 4-substituted benzocyclobutene should give the *ortho*- and *meta*-substituted styrenes. Thus, our



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

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

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(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.

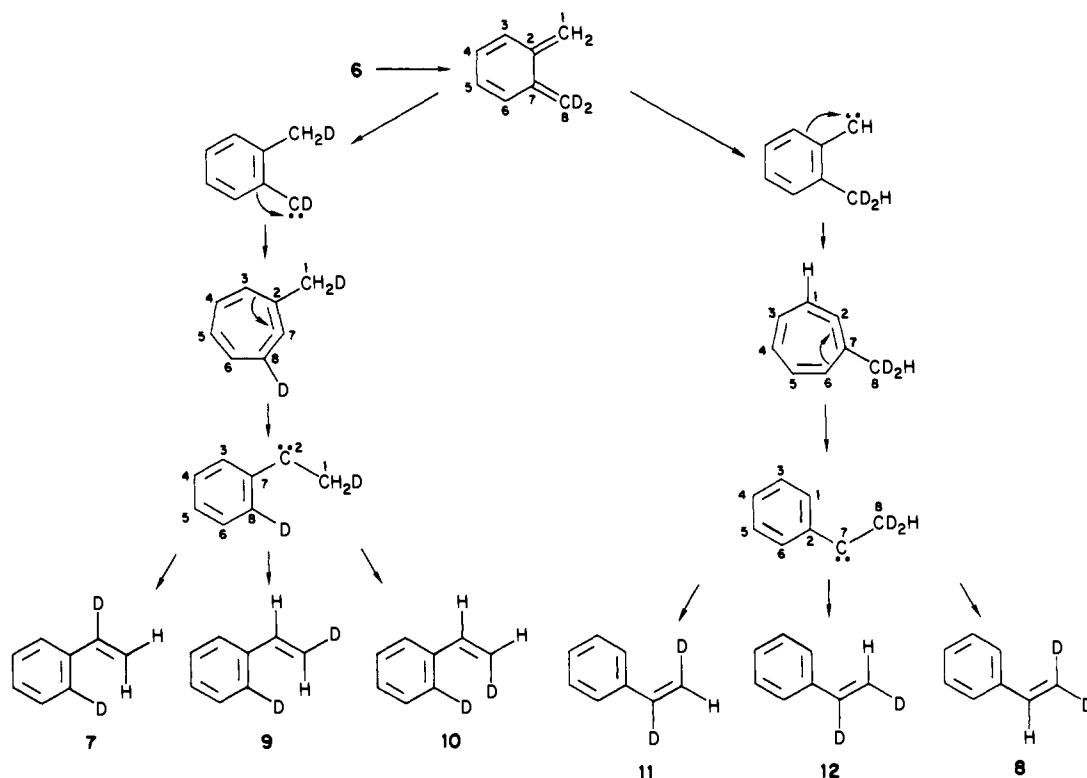
(1) Trahanovsky, W.; Scribner, M. "Abstracts of Papers", 186th Meeting of the American Chemical Society, Washington, DC, Aug 1983; American Chemical Society: Washington, DC, 1983; ORGN 57.

(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.

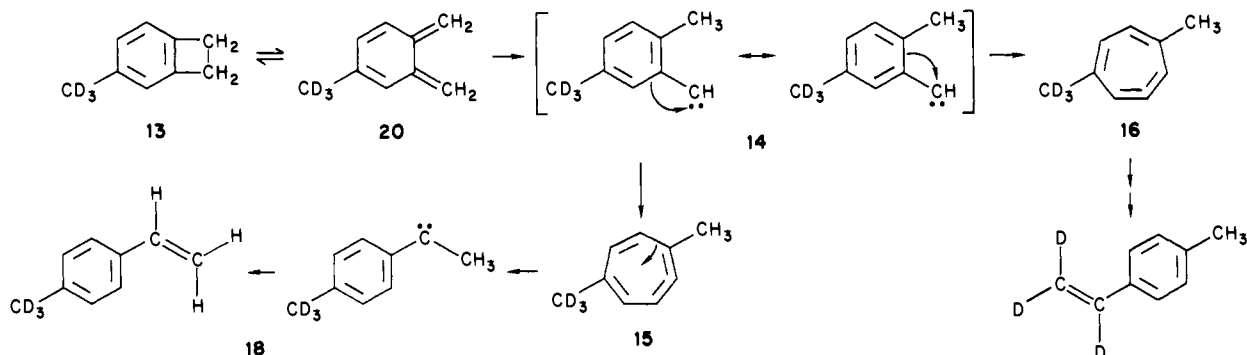
(3) (a) McCullough, J. J. *Acc. Chem. Res.* 1980, 13, 270-276 and references cited therein. (b) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* 1980, 41-61.

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

Scheme I



Scheme II

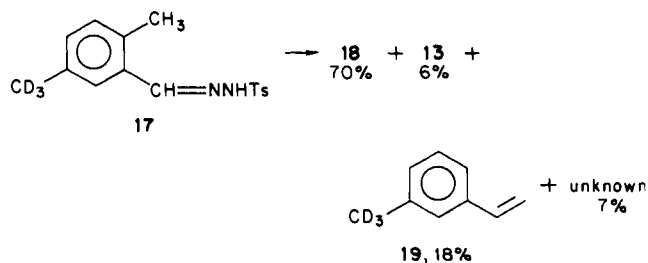


hydrogen shifts, indicate that there are kinetic isotope effects. Calculation shows that the yields of 7 and 8 and the combined yields of 9 to 12 are accounted for by an isotope effect of 2.5 for each step. In agreement with this, we have observed that in the rearrangement of $\text{CH}_2\text{D}-\dot{\text{C}}-\text{Ph}$ and $\text{CHD}_2-\dot{\text{C}}-\text{Ph}$, generated by pyrolysis of the tosylhydrazone at 800 °C, the isotope effect is ca. 2.1.

In Scheme I, each of the *o*-tolylcarbenes is converted to only one of two possible cycloheptatetraenes. Conversion to the other cycloheptatetraene moves the 7- or 2-carbon atom away from the methyl group, and a series of cycloheptatetraene-arylcabene interconversions can move this atom around the ring eventually forming the same α -methylphenylcarbene produced by the route shown in Scheme I. For the parent system, this alternative set of cycloheptatetraene-arylcabene interconversions results in no new stable product, but for a methyl-substituted benzocyclobutene, this pathway would incorporate the substituent methyl group into the vinyl portion of the styrene. Thus, we pyrolyzed 13.¹² Scheme II shows both sets of interconversions for one of the arylcarbenes formed initially from 13. The other arylcarbene would give rise to the deuterated *m*-methylstyrenes.

Pyrolysis (850 °C) of 13 gave comparable amounts of *m*- and *p*-methylstyrenes, as was obtained from 5, and both ¹H and ²H

NMR analysis showed deuterium in the methyl groups only. This means that only one of the two possible cycloheptatetraenes, 15, is formed from carbene 14. This conclusion was confirmed by generating 14 from tosylhydrazone 17¹³ and observing again that no deuterium was incorporated into the vinyl group of the expected product *p*-methylstyrene. A possible explanation for the pref-



erential formation of 15 from 14 is that, in the formation of 15, the carbene carbon of 14 moves away from the *o*-methyl group,

(13) The melting point of 17 matched that reported for undeuterated tosylhydrazone¹⁴ and a satisfactory IR and ¹H NMR spectra and elemental analysis were obtained for 17. The pyrolysis (800 °C) of 17 was carried out by the previously described hot-tube technique.¹⁴

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

(12) Compound 13 was prepared from 4-carbomethoxybenzocyclobutene.

but in the formation of **16**, the carbene carbon moves toward the *o*-methyl group. Products **13** and **19** show that the first few steps of the mechanism in Scheme I are reversible and that carbene **14** can close to **13** or undergo a hydrogen transfer to give the *o*-quinodimethane **20** and that some of **13** or **20** can rearrange to **19**.

Thus the results of our labeling experiments are consistent with the conclusion that the major pathway for the rearrangement of **1** to **2** involves a series of arylcarbene-cycloheptatetraene interconversions.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, Budget Code AK-01-03-021, under Contract W-7405-ENG-82. We thank Professor Champman and his co-workers for sending us their results prior to publication and W. S. Trahanovsky, Jr., for computational assistance.

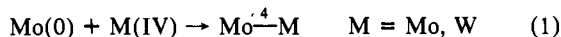
Use of η^6 -Arylphosphine Complexes of Molybdenum(0) for the Synthesis of Complexes Containing Mo⁴-Mo and Mo⁴-W Bonds

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Received August 14, 1984

The three heterobimetallic complexes known to have quadruple metal-metal bonds are CrMo(O₂CMe)₄,¹ MoW(O₂CCMe₃)₄,² and MoW(mhp)₄.³ In each case the quadruple bonds are bridged by bidentate ligands: acetate, pivolate, or 2-hydroxy-6-methylpyridine anion, respectively. Complexes containing the homonuclear quadruple bonds Mo⁴-Mo or W⁴-W with and without bridging ligands have been well studied,⁴ including complexes Mo₂Cl₄(PR₃)₄⁵⁻⁹ and W₂Cl₄(PR₃)₄^{5,10,11} where PR₃ is a tertiary phosphine ligand. We report here the very efficient synthesis of MoWCl₄(PMePh₂)₄, which contains the first heterobimetallic quadruple bond that is not supported by bridging ligands. The properties of this bond can be compared for the first time with Mo⁴-Mo and W⁴-W bonds that are free of bridging ligands. Our synthesis of MoWCl₄(PMePh₂)₄ involves two novel features: first, the reaction of a mononuclear complex of Mo(0) with chloride compounds of Mo(IV) or W(IV) to give Mo⁴-M dimers (eq 1);



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Scheme I

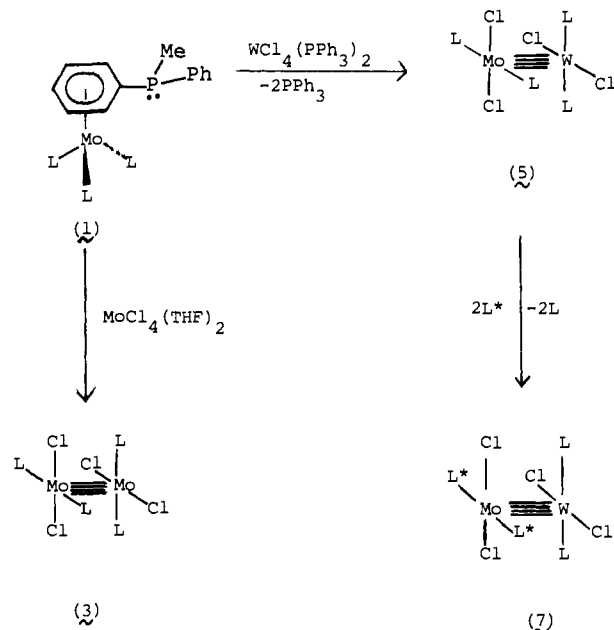


Table I. ³¹P NMR Data for **5** (in C₆H₆ vs. 85% H₃PO₄) and W₂Cl₄P₄ (**6**),¹⁰ P = PMePh₂

isotopomer	δ(³¹ P), ppm	J _{PP} ³ , Hz	J _{PW} ² , Hz	J _{PW} ¹ , Hz
W ⁴ -Mo-P	-13.1 t	23.5		
¹⁸³ W ⁴ -Mo-P	-13.1 dt	23.5	43	
P-W ⁴ -Mo	21.9 t	23.5		
P- ¹⁸³ W ⁴ -Mo	21.9 dt	23.5		266
¹⁸³ W ⁴ -W (6)	2.0 m	28	51	234

second, the use of a Mo(0) complex containing an η^6 -PhPMePh ligand to give a Mo⁴-M compound in a regiospecific reaction.

During our study of the use of derivatives of Mo(η^6 -PhPMePh)(PMePh₂)₃ (**1**) as phosphine-like ligands,¹² we discovered that complex **1** reacted with MoCl₄(THF)₂¹³ (**2**) after stirring for 10 h in degassed tetrahydrofuran (THF) at 22 °C to give the known complex Mo₂Cl₄(PMePh₂)₄^{7,14} (**3**) in its green form¹⁴ (Scheme I). Precipitation with hexanes and recrystallization from benzene/hexanes gave **3** as its blue isomer¹⁴ in 75% yield. The dinitrogen complex *trans*-Mo(N₂)₂(PMePh₂)₄ also reacted with **2** to give **3**. Complex **3** was identified by C, H analysis and ³¹P NMR.¹⁴ The blue isomer in benzene had a visible absorption (δ → δ*) at 596 nm and a Raman active mode, ν-(Mo⁴-Mo), at 349 cm⁻¹ in agreement with literature values.¹⁴

The new complex MoWCl₄(PMePh₂)₄ (**5**)¹⁵ is prepared according to Scheme I by adding a benzene solution of **1** dropwise to a 3-fold excess of WCl₄(PPh₃)₂ (**4**)¹⁶ suspended in dry benzene under N₂. The reaction is instantaneous at 22 °C; excess **4** is filtered off after 5 min and green complex **5**, contaminated with approximately 5% **3**, is crystallized with hexanes. Complex **3** is the only detectable side product; however, if traces of water are present then side reactions give WOCl₂(PMePh₂)₃¹⁷ as well as complex **3**. Complex **3** cannot be separated from **5** by chromatography, but **3** can be fairly selectively converted by reaction with

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