

were made for absorption or anomalous dispersion, but a secondary extinction correction was applied.

The molecular geometry and the numbering system are shown in three-dimensional stereopair diagrams in Figures 1 and 2 for I and II, respectively. In both molecules the cyclohexylidene system adopts the familiar chair conformation whereby the 2-phenyl substituent assumes the axial position required by the theory of  $A^{(1,3)}$  strain.<sup>2</sup> That these chairs conform closely to the geometry reported<sup>5-7</sup> for cyclohexane and its substituted derivatives is indicated by the average torsion angles about the C-C bonds ( $55.3$  and  $53.5^\circ$  for I and II, respectively) which are within the range ( $52.9$ – $57.1^\circ$ ) observed for cyclohexane derivatives.<sup>5-7</sup> The spread of their individual values in I, from  $54.2 \pm 0.4$  to  $56.8 \pm 0.4^\circ$ , is not larger than in disubstituted cyclohexanes,<sup>7</sup> but some distortions from "normal" chair geometry may be present in II, where the torsion angles range from  $49.0 \pm 0.3$  to  $59.6 \pm 0.3^\circ$ . The average internal bond angles at  $sp^3$ -hybridized carbon atoms ( $110.7$  and  $111.1^\circ$  for I and II, respectively) compare well with values observed for cyclohexanes.<sup>5-8</sup> The internal C(2)–C(1)–C(6) angles at the  $sp^2$ -hybridized carbon atoms are  $114.0 \pm 0.3^\circ$  for I, and  $115.0 \pm 0.2^\circ$  for II.

In both isomers the axial phenyl group lies symmetrically above the ring in a manner which minimizes the nonbonded interactions between its ortho hydrogen atoms and the 4- and 6-axial hydrogens of the cyclohexylidene system (1,3-diaxial interactions). This geometry allows an ortho hydrogen atom to approach the 3-equatorial hydrogen fairly closely however, and results in contacts of  $2.07 \pm 0.04 \text{ \AA}$  for H(15)···H(32) in I, and  $2.07 \pm 0.03 \text{ \AA}$  for H(19)···H(32) in II.

An interesting difference in bond lengths occurs for the two types of C( $sp^2$ )–O single bonds in these structures: the C(20)–O(22) bonds average  $1.365 \text{ \AA}$  and apparently contain double character. They are substantially shorter than the C(7)–O(22) bonds which average  $1.424 \text{ \AA}$ . The latter value might represent a good approximation to the C( $sp^2$ )–O single bond since conventional resonance structures exclude double character in these bonds. Also, certain differences in conformation occur between I and II. C(7) is nearly coplanar with the acetoxy group in both molecules, and these planes form an angle of  $81^\circ$  in I and  $88.9^\circ$  in II with the planes are defined by {C(1), C(7), O(22)}. Although O(23) is cis to C(7) in both syn and anti isomers, twisting around C(7)–O(22) is in the opposite sense so that the acetoxy group is rotated toward the axial side of the cyclohexylidene system in I, but toward its equatorial side in II. The phenyl substituted at the double bond and the plane defined by {C(1), C(7), and C(8)} are not coplanar, but form a dihedral angle of  $45.5^\circ$  in I and  $88.5^\circ$  in II. The C(7)–C(8) bond lengths ( $1.471 \pm 0.004$  and  $1.484 \pm 0.003 \text{ \AA}$  for I and II, respectively) reflect the resulting absence of conjugation between the double bond and the aromatic system.

Small but significant distortions from planarity are observed in the unsaturated system formed by the exocyclic double bond. These distortions, which

originate partly from nonplanarity at C(1) and C(7), and partly from twisting around the double bond, relieve nonbonded interactions of C(8) and O(22) with equatorial hydrogen atoms at C(2) and C(6), and will be discussed in detail in a future publication. Even further separation of C(8) and the 6- or 2-equatorial hydrogen is achieved by opening the C(1)–C(7)–C(8) angle to  $130.1 \pm 0.3$  and  $127.7 \pm 0.2^\circ$  in the anti and syn isomers, respectively.

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### Silver(I) Ion Catalyzed Rearrangements of Strained $\sigma$ Bonds. VIII. Deuterium Isotope Effects in the Bond Reorganizations of Tricyclo[4.1.0.0<sup>2,7</sup>]heptanes<sup>1</sup>

Sir:

Previously, structural considerations were advanced in support of the hypothesis that interaction of  $Ag^+$  with bicyclobutanes leads in certain cases to argento carbonium ions. This particular mechanism, which requires the rupture of one edge bond and the central bond, was considered to be competitive with an alternative pathway involving the stepwise cleavage of two diametrically opposed edge bonds. The anticipated dependence of these carbonium ion mechanisms on appropriate incremental alkyl substitution of the bicyclobutane ring is most strikingly exhibited by tricyclo[4.1.0.0<sup>2,7</sup>]heptane derivatives. For example, whereas **1a** gives rise quantitatively to *cis,cis*-1,3-cycloheptadiene (**2a**),<sup>2,3</sup> monomethyl derivative **3a** produces in 96% yield a mixture of four isomeric hydrocarbons when treated similarly with  $AgClO_4$  in benzene at  $40^\circ$ .<sup>1</sup> We have presently obtained deuterium isotope effect data on **1** and **3** which now make manifest the intimate details of these bond reorganizations.

Whereas the rearrangement of **1a** at  $40^\circ$  in an azeotropically dried benzene solution of silver perchlorate (0.0845 *N*) proceeded with a rate constant of  $2.27 \pm 0.03 \times 10^{-3} \text{ M sec}^{-1}$ , its dideuterio analog **1b** exhibited a substantially *faster* rate of isomerization ( $2.68 \pm 0.01 \times 10^{-3} \text{ M sec}^{-1}$ ), thereby giving rise to an *inverse* isotope effect (Table I). Similar rearrangement of **3a**

Table I. Deuterium Isotope Effect Data

Tricycloheptane	Product	$k_H/k_D$
<b>1</b>	<b>2</b>	0.847
<b>3</b>	<b>4</b> and <b>5</b>	0.95
	<b>6</b>	0.91
	<b>7</b>	1.74
<b>3'</b>	<b>4'</b> and <b>5'</b>	1.21
	<b>6'</b>	0.99
	<b>7'</b>	1.03

(1) For paper VII of this series, see L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 2335 (1971).

(2) (a) L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *ibid.*, **92**, 7002 (1970); (b) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **93**, 1288 (1971).

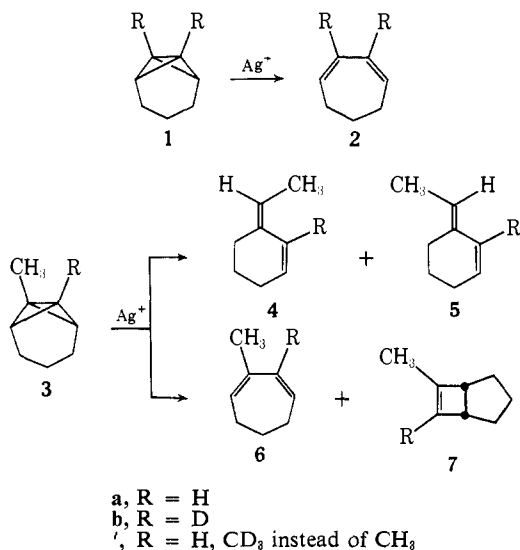
(3) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, **93**, 1043 (1971).

(5) J. D. Dunitz and P. Strickler, *Helv. Chim. Acta*, **49**, 2502 (1966).

(6) J. D. Dunitz and P. Strickler, *ibid.*, **49**, 2505 (1966).

(7) F. P. van Remoortere and F. P. Boer, *J. Chem. Soc.*, in press.

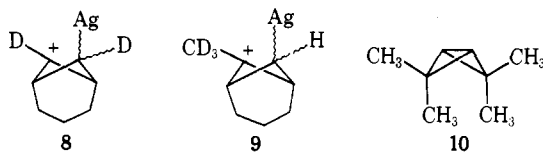
(8) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).



to low (7–8%) conversion yielded a mixture composed of 29.3% of ethylidenecyclohexenes **4a** and **5a**,<sup>4</sup> 26.4% of 2-methyl-1,3-cycloheptadiene (**6a**), and 44.3% of 6-methylbicyclo[3.2.0]hept-6-ene (**7a**).<sup>2b</sup> When deuterated substrate **3b** was isomerized, the combined yield of **4b** and **5b** rose reproducibly to 34.9%. The proportion of **6b** also increased (35.3%), but the amount of **7b** dropped dramatically to only 29.8%. The *inverse* secondary deuterium isotope effects noted in the formation of dienes **4–6** (Table I) clearly parallel the precedent established by **1b**. It is important to note, however, that the values for **4–6** are more positive than for **1b** in addition to being quite similar to each other in relative magnitude; also, multiplication of the isotope effect for the formation of **6** by that associated with **4** and **5** gives a product (0.865) nearly identical with the isotope effect exhibited by **2** (0.847). Most interestingly, the production of **7** is subject to a primary deuterium isotope effect (1.74) in agreement with the concept that it arises uniquely from a more deep seated skeletal rearrangement.<sup>2b</sup>

Similar treatment of **3'** resulted in a significant *decrease* in the yields of **4'** and **5'**. The magnitude of this isotope effect (1.21) requires that the CD<sub>3</sub> group have occasion to exert its nearly limiting rate-retarding effect during the conversion of **3'** to the ethylidenecyclohexenes. On the other hand, the mechanistic pathways leading to **6'** and **7'** exhibit virtually nil isotope effect with this particular labeling pattern.

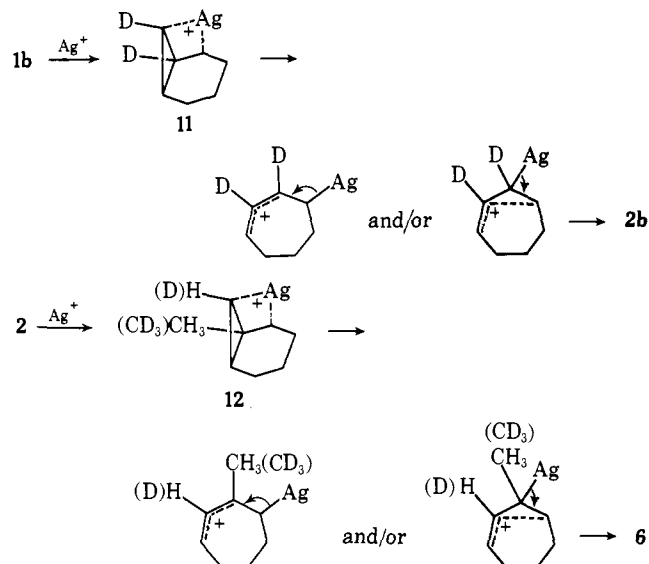
The above results reveal that the mechanistic pathway leading to 1,3-cycloheptadiene derivatives cannot involve initial central bond cleavage. Although  $k_H/k_D$  for **8** is difficult to estimate, that for **9** is clearly not



to a related diene type<sup>1)</sup> is not rationalizable in these terms.

Rather, the evidence can best be explained in terms of a model in which an edge bicyclobutane bond is first severed (Scheme I). In the case of **3**, this bond is

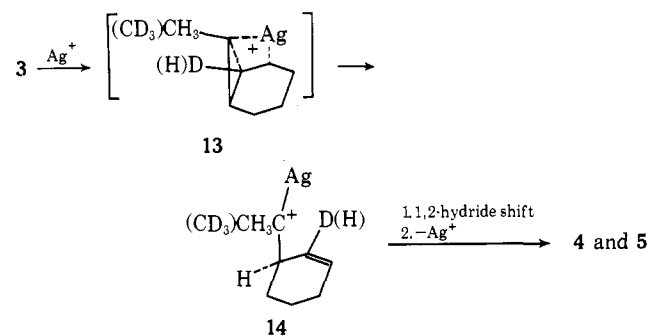
#### Scheme I. Mechanistic Considerations underlying Cycloheptadiene Formation



required to be that which is remote from the methyl substituent. The inverse isotope effects are consequently related directly to the enhancement of the C–H bending force constants which accompany the structural change from the tricycloheptanes to **11** and **12**.<sup>5,6</sup> Ring opening (two possible routes) of the coordinated cyclopropyl cation present in these intermediates, followed by loss of Ag<sup>+</sup>, leads to the cycloheptadienes. Argentocarbonium ions are by-passed in these instances, presumably because of their secondary nature.

Oxidative addition of Ag<sup>+</sup> to a more highly substituted edge bond in **3** properly accommodates ethylidenecyclohexene formation (Scheme II). In particular,

#### Scheme II. Mechanistic Considerations underlying Ethylidenecyclohexene Formation



the substantial isotope effect exhibited by **4'** and **5'** (1.21) cannot be due solely to the inductive effect of

reconcilable with a value of 0.99. Furthermore, the rate of production of **6a** is *slower* than for **2a**. Also, the driving force underlying the 10<sup>4</sup>-fold rate acceleration (*vs.* **1**) exhibited by **10** (which rearranges exclusively

(4) A syn:anti ratio of 4:1 was observed. This ratio remained invariant starting with either **3a**, **3b**, or **3'**.

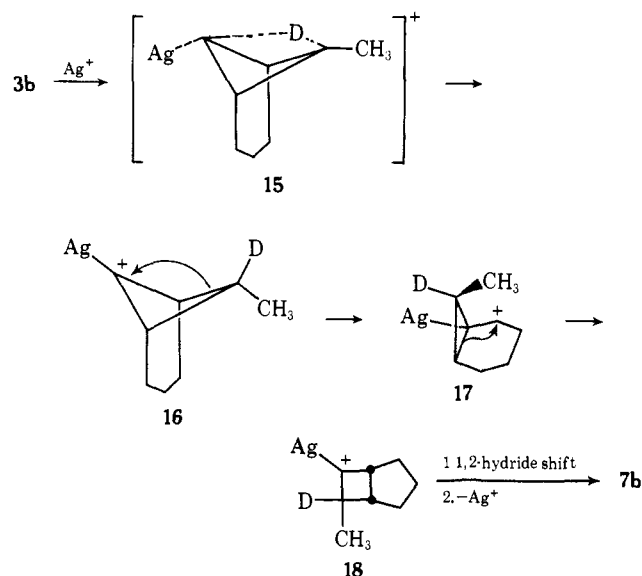
(5) Infrared and Raman spectral studies have confirmed the increased translational, vibrational, rotational, etc., partition functions of cyclopropyl hydrogens relative to the bridgehead hydrogens in **1**. These results will be described in our full paper.

(6) The rehybridization at the carbons bearing deuterium may be approximated as 40% s → ~30% s character [G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963)].

a somewhat remote cationic site. Rather, the result is in keeping with a hyperconjugative effect at a highly developed electrophilic center. Simultaneous edge and central bond cleavage is therefore proposed. Because transition state **13** resembles tertiary argento carbonium ion **14** structurally, substantial positive character should reside on the carbon bearing the CD<sub>3</sub> (CH<sub>3</sub>) substituent. This mechanism bears many similarities to a reverse carbenoid addition to a double bond. The fractionation factor exhibited by **4b** and **5b** (0.95) is likewise in accord with Scheme II. Since only one deuterium atom is involved, the total observable impact of the effect of isotopic substitution should understandably be less than that experienced by **2b**.

Lastly, we address ourselves to the primary isotope effect experienced by **7**. The magnitude of this effect (1.74) indicates that the bridgehead C-H or C-D bond is either weakly or extensively stretched at the transition state. In view of the very small fractionation factor shown by **7'** (1.03), the latter alternative appears uniquely reasonable (*cf.* **15**, Scheme III). Furthermore,

Scheme III



the geometry associated with this 1,3-hydride shift is sufficiently nonlinear that only a low  $k_{\text{H}}/k_{\text{D}}$  value can be expected on the basis of recent theoretical calculations.<sup>7</sup> The driving force for the deuteride (hydride) shift can be thought of as being due principally to the generation of argento carbonium ion **16**. Rearrangement of **16** to **17** appears to be followed by internal cyclopropyl bond migration (rather than cleavage) because of the compensating gain in stabilization derivable from newly generated bicyclic argento carbonium ion **18**. The conversion of **18** to **7** follows a well-recognized pathway. Additional ramifications of this novel kinetically controlled hydrogen transfer are being sought.

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(7) R. A. More O'Ferrall, *J. Chem. Soc. B*, 785 (1970).

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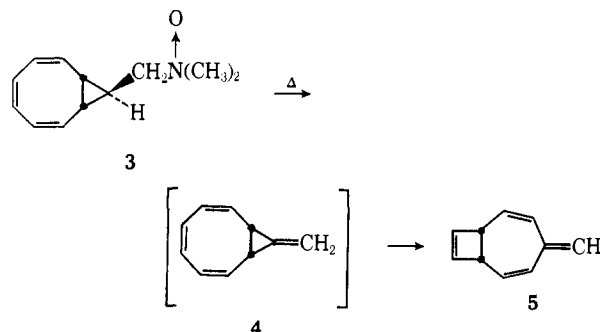
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### The *cis*-Bicyclo[5.2.0]nona-2,5,8-triene to *cis*-Bicyclo[6.1.0]nona-2,4,6-triene Rearrangement. Elucidation of the Relative Efficiencies of *Syn*-Disposed Cyclopropane and Cyclobutene Ring Cleavages during Azo Decomposition

Sir:

The mechanisms by which *cis*-bicyclo[6.1.0]nona-2,4,6-trienes (**1**) undergo thermal rearrangement to 8,9-dihydroindenes have been the object of much discussion in the current literature.<sup>1</sup> Several groups have recently considered the possibility that such bond reorganizations may be triggered in certain instances by initial [3,3] sigmatropic rearrangement to *cis*-bicyclo[5.2.0]nona-2,5,8-trienes (**2**).<sup>2</sup> Despite the fact that there exists some evidence that the bicyclo[6.1.0]nonatriene ring system may be capable of kinetically controlled Cope rearrangement to a [5.2.0]bicyclo counterpart,<sup>3</sup> the behavior of **4** (not interceptable) is likely to be atypical because of the destabilization accorded this triene by the exocyclic methylene group.<sup>4</sup>



To the present time, **5** represents the only known derivative of **2**. In an attempt to remove this hiatus and simultaneously obtain evidence on the chemical behavior of this novel polyenic system, a synthesis of the 2,6-diphenyl derivative **9** has been developed. The route of **9** is of interest because it also provides unequivocal demonstration of the fact that cleavage of a cyclopropyl bond is kinetically preferred to that of an internal cyclobutene  $\sigma$  bond when both rings are aligned *syn* to departing nitrogen in a tetracyclic azo compound **8**.

Ceric ion oxidation of cyclobutadieneiron tricarbonyl (**7**)<sup>5</sup> in the presence of 2,5-diphenyl-3,4-diazanorcaradiene (**9**) has been developed.

(1) J. C. Barborak, T.-M. Su, P. v. R. Schleyer, G. Boche, and G. Schneider, *J. Amer. Chem. Soc.*, **93**, 279 (1971), and references cited therein.

(2) (a) P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969); (b) A. G. Anastassiou and R. C. Griffith, *ibid.*, **93**, 3083 (1971).

(3) P. Radlick, W. Fenical, and G. Alford, *Tetrahedron Lett.*, 2707 (1970).

(4) The estimated strain-energy difference between methylene-cyclopropane (41.7 kcal/mol) and cyclobutene (30.6 kcal/mol) reflects the magnitude of this effect (*ca.* 11.1 kcal/mol): P. v. R. Schleyer, J. E. Williams, and K. L. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).