

# Mechanistic Aspects of the Silver(I)-Promoted Rearrangements of Tricyclo[4.1.0.0<sup>2,7</sup>]heptane Derivatives. Deuterium Isotope Effect Studies and Independent Generation of Argento Carbonium Ions<sup>1,2</sup>

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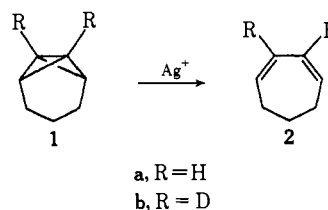
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**Abstract:** Kinetic deuterium isotope effects have been determined for the Ag<sup>+</sup>-catalyzed rearrangements of 1,7-dideuterio- (**1b**), 1-deuterio-7-methyl- (**3b**), and 1-trideuteriomethyltricyclo[4.1.0.0<sup>2,7</sup>]heptanes (**8**). Dideuterio analog **1a** exhibited a faster rate of isomerization to 1,3-cycloheptadiene-2,3-*d*<sub>2</sub> than its protio counterpart, thereby giving rise to an inverse fractionation factor ( $k_H/k_D = 0.847$ ). A similar rearrangement of **3b** revealed that the isomeric ethylenecyclohexenes **4b** and **5b** as well as 2-methylcycloheptadiene **6b** were also produced under the control of inverse isotope effects ( $k_H/k_D = 0.95$  and  $0.91$ , respectively). Most interestingly, the formation of bicyclo[3.2.0]heptene **7b** is subject to a virtual primary deuterium isotope effect (1.74). In the case of **8**, the mechanistic pathways leading to **11** and **12** exhibit virtually nil isotope effect, whereas the -CD<sub>3</sub> group markedly influences the  $k_H/k_D$  affecting the ethylenecyclohexenes **9** and **10** (1.21). The mechanistic implications of the isotope data are discussed, and suggested pathways are advanced to account for the genesis of the various products.

Completion of the tricyclo[4.1.0.0<sup>2,7</sup>]heptane (**1a**) isomerization study<sup>1,4</sup> left little doubt that Ag(I)-promoted rearrangement of bicyclobutane derivatives was to be a fascinating and fruitful area of research. Further, it was evident that the strain factor, although of paramount importance, was not the sole controlling influence in the diversified bond reorganizations which certain derivatives of **1a** undergo. A most significant development was recognition that such catalyzed rearrangements exhibit in particular a marked dependence on the position of alkyl substitution. It soon became evident that acquisition of definitive evidence relating to the mechanisms of these transformations would require a more detailed physical organic treatment. Thus, in our pursuit of satisfactory mechanistic rationales for the formation of 1,3-cycloheptadienes, alkylidenecyclohexenes, and bicyclo[3.2.0]heptenes, we initiated an examination of deuterium isotope effects. Herein we report the details of this investigation which has in part resolved the issues central to the subject.

**Measurement of Isotope Effects.<sup>5</sup>** The quantitative rearrangement of **1a** to 1,3-cycloheptadiene (**2a**) at 40.00° in an azeotropically dried benzene solution of silver perchlorate (0.0845 *N*) has previously been shown to proceed with a rate constant of  $2.27 \pm 0.03 \times 10^{-3}$

$M^{-1} \text{ sec}^{-1}$ .<sup>1</sup> Interestingly, the 1,7-dideuterio analog **1b** exhibits isomerization under identical conditions at a substantially faster rate ( $2.68 \pm 0.01 \times 10^{-3} M^{-1}$



$\text{sec}^{-1}$ ). Thus, incorporation of two deuterium atoms at the indicated positions gives rise to an *inverse* isotope effect ( $k_H/k_D$ ) of 0.847.

For practical reasons, the detailed behavior of **3a** and its deuterated counterparts **3b** and **8** was elucidated by quantitative gas chromatographic analysis of product compositions. In all instances, vpc response factors were determined with independently prepared solutions of accurately known concentrations. Mesitylene was employed as the internal standard. Because of the near identity of the vpc retention times of **7a** and **7b** with those of **3a** and **3b**, respectively, under the conditions employed, per cent composition data for these bicycloheptanes were determined only after completion of the rearrangement. With regard to **3a**, exposure to 0.0845 *N* AgClO<sub>4</sub> in anhydrous benzene as before for periods of low (7–8%) conversion yielded a mixture composed of 29.3% of **4a** and **5a**,<sup>6</sup> 26.4% of **6a**, and 44.3% of **7a**.<sup>1</sup> When monodeuterated substrate **3b** was identically isomerized, the combined yield of **4b** and **5b** increased reproducibly to 34.9%. The proportion of **6b** also rose (35.3%), but the amount of **7b** declined dramatically to only 29.8%!

The *inverse* secondary deuterium isotope effect noted in the formation of **6** ( $k_H/k_D = 0.91$ ), as expected, parallels that found earlier for **2**. The value is more positive, presumably because only one deuterium atom is

(6) A syn:anti ratio of 4:1 was observed. This ratio remained invariant starting with either **3a**, **3b**, or **8**.

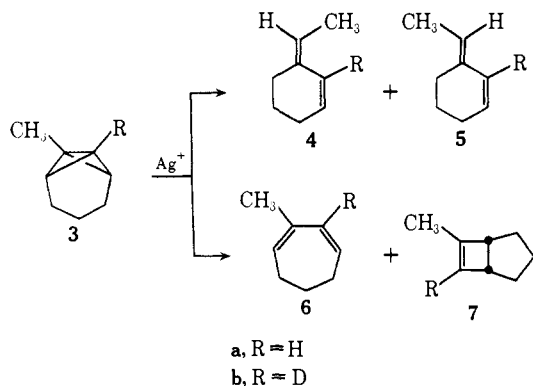
(1) Part XIII of the series dealing with Ag<sup>+</sup>-catalyzed rearrangements. For the previous paper, see L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, **94**, 7761 (1972).

(2) Various aspects of this work have been presented at the Meeting of the Chemical Institute of Canada, Halifax, Nova Scotia, May 1971, the 22nd National Organic Chemistry Symposium, Ann Arbor, Mich., June 1971, and the Second Belgian Chemical Society Symposium on Small Rings and Activated Multiple Bonds, Louvain, Belgium, Sept 1971.

(3) (a) National Institutes of Health Postdoctoral Fellow, 1970–1971; National Science Foundation Postdoctoral Fellow, 1971–1972; (b) National Science Foundation Graduate Trainee, 1970–1972.

(4) Previous communications by this group on this particular subject are: (a) L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Amer. Chem. Soc.*, **92**, 7002 (1970); (b) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **93**, 1288 (1971); (c) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971).

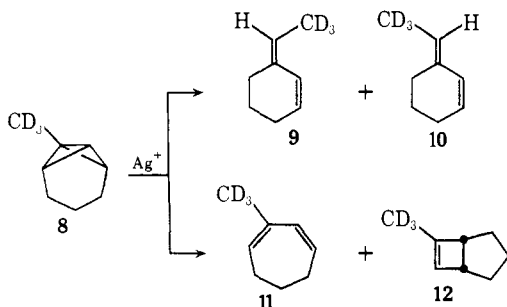
(5) The essentials of this work have been summarized earlier: L. A. Paquette and S. E. Wilson, *ibid.*, **93**, 5934 (1971).



now affected. These data are in agreement with the concept that similar structural changes have taken place at the isotopically substituted positions in **1** and **3** as these tricycloheptanes proceed along the reaction coordinate to the respective transition states which give rise to the 1,3-cycloheptadienes. Replacement of C<sub>7</sub>-H by deuterium in **3** also imparts an *inverse* isotope effect ( $k_H/k_D = 0.95$ ) to the production of ethylenecyclohexenes **4** and **5**. As before, the primary cause of the rate increases in **3b** must be loss of s character in the external bond to C<sub>7</sub> at the transition state of kinetic consequence. It is interesting and mechanistically relevant that 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).<sup>7</sup>

Of particular significance was the observation that the production of **7** is subject to a virtual *primary* deuterium isotope effect ( $k_H/k_D = 1.74$ ). Although we recognized earlier that such bicycloheptenes were very likely the result of deep-seated skeletal rearrangements,<sup>4b</sup> we were somewhat surprised to note that the actual isomerization involves a fractionation factor the magnitude of which suggests pronounced perturbation of the bridgehead C-H (or C-D) bond.

Treatment of **8** with the identical silver perchlorate-benzene solution under comparable conditions resulted in a notable decrease in the yield of **9** and **10** (25.8%).<sup>6</sup> 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 **8** to the labeled ethylenecyclohexenes. On the other hand, the mechanistic pathways leading to **11** ( $k_H/k_D = 0.99$ ) and **12** ( $k_H/k_D = 1.03$ ) exhibit virtually a

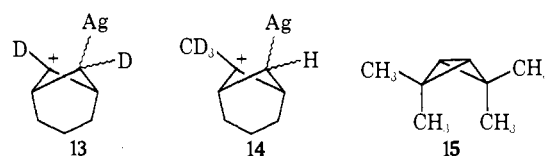


nil isotope effect with this particular deuterium substitution pattern.

(7) For a discussion of the conditions under which multiplicative isotope effects apply, consult E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964, p 210.

The combination of product structure considerations<sup>1</sup> and the above experimental data strongly limit the number of plausible mechanistic possibilities. All the isotope effects are secondary in nature except seemingly for that leading to **7**, but bicycloheptene formation is recognized to be the result of bridgehead substitution. Consequently, these two effects must be accommodated by the final mechanism.

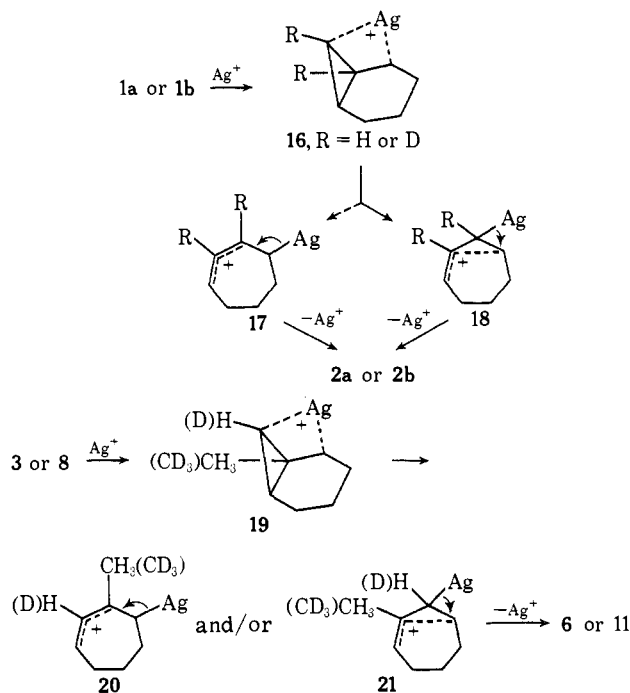
**The Pathway to 1,3-Cycloheptadienes.** Our results show that 1,3-cycloheptadiene derivatives cannot arise from initial central bond cleavage. Although a theoretical value of  $k_H/k_D$  for **13** is somewhat difficult to estimate, that for **14** is decidedly not reconcilable with a value of 0.99. In the latter event, hyperconjugation of the -CD<sub>3</sub> group is expected to be geometrically permissible in the transition state with the result that a sub-



stantial positive isotope effect should be encountered. Such is not observed. Additionally, the rate of appearance of **6a** is *slower* than for **2a**;<sup>1</sup> if **14** were involved, the rate enhancing property of the methyl group should be in evidence, and it is not. Furthermore, the driving force underlying the 10<sup>4</sup>-fold rate acceleration (*vs.* **1a**) exhibited by **15** (which rearranges exclusively to a related diene type)<sup>4c,8</sup> is not rationalizable in these terms.

Rather, all available evidence can best be reconciled in terms of a model in which an edge bicyclobutane bond is first severed (Scheme I). In the case of **3** and **8**,

Scheme I



oxidative addition of Ag<sup>+</sup> is required to occur at one of the two bonds remote from the methyl substituent (*cf.* **19**). As will be seen below, attack of Ag<sup>+</sup> on the more

(8) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **94**, 7780 (1972).

hindered surface leads to ethylenecyclohexene formation. In this regard, the very similar yields of **6a** and **4a-5a** reveal that neither bond cleavage mode is overwhelmingly preferred.

The operation of an inverse isotope effect on the generation of 1,3-cycloheptadienes must consequently be related directly to enhancement of the C-H bending force constants which accompany the structural change from the tricycloheptanes to the norcarane-like intermediates **16** and **19**. In actuality, rehybridization at the carbons bearing deuterium during such a ring opening may be approximated as 40%  $s^p \rightarrow \sim 30\%$   $s$  character. Indeed infrared and Raman spectral studies have confirmed the increased vibrational partition functions involving cyclopropyl hydrogens (as in **16** and **19**) relative to the bridgehead hydrogens in **1** (Table I). It is most likely, therefore, that substitution

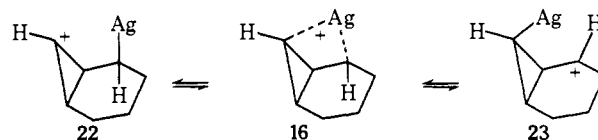
Table I. Stretching Frequencies of Various C-H Bonds

Compound	Pertinent hybridization	Band, $\text{cm}^{-1}$		Ref
		Infrared	Raman	
$\text{CH}_3\text{-CH}_3$	$\text{sp}^3$ C-H	2995 2954	2963, 2940 2899	a,b
$\triangle$	$\text{sp}^{2.28}$ C-H <sup>a</sup>	3103 3028	3082 3038, 3028	c
$\text{D}_2$ $\text{D}_2 \triangle \text{D}_2$	$\text{sp}^{2.28}$ C-H <sup>a</sup>	2336 2211	2329 2236, 2211	c
$\text{H}_2\text{C=CH}_2$	$\text{sp}^2$ C-H	3105 2989	3019	d
	$\text{sp}^{1.46}$ C-H <sup>i</sup>	3096	3105	e
	$\text{sp}^{1.46}$ C-H <sup>i</sup>	2284	2338	e
$\text{HC}\equiv\text{CH}$	$\text{sp}$ C-H	3282	3374	f,g

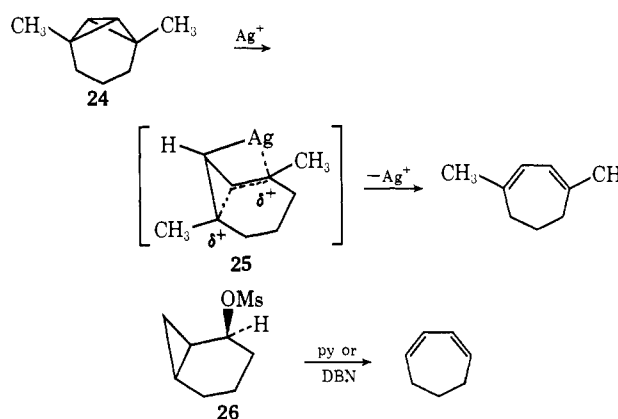
<sup>a</sup> G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, p 344. <sup>b</sup> L. G. Smith, *J. Chem. Phys.*, **17**, 139 (1952). <sup>c</sup> S. J. Cyvin, *Spectrochim. Acta*, **16**, 1022 (1960). <sup>d</sup> See footnote a, p 326. <sup>e</sup> This work. <sup>f</sup> E. E. Bell and H. H. Nielsen, *J. Chem. Phys.*, **18**, 1382 (1950). <sup>g</sup> H. C. Allen, E. D. Tidwell, and E. K. Plyler, *J. Res. Nat. Bur. Stand.*, **57**, 213 (1956). <sup>h</sup> L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., p 518. <sup>i</sup> Z. Maksić, J. M. Jerkunica, and D. Stefanović, *Croat. Chlm. Acta*, **38**, 49 (1966).

of deuterium for hydrogen as in **3** leads to an enhancement of the rate of formation of **6** chiefly as a consequence of a substantial hydrogen force constant change in the transition state leading to **19**. The observed fractionation factor for **1** (0.847) is actually a composite of the same  $\alpha$  effect and an added  $\beta$  effect. Both sites do experience alteration of their hybridization status, but the two C-D bond orders in **16** are not expected to be identical. The negligible isotope effect observed with **8** (0.99) is entirely compatible with the model since in **19** (and its respective transition state) the trideuteriomethyl group is effectively insulated from the reaction site.

This leads us to a consideration of the structural features of **16** and its subsequent rearrangement. We have taken into account the possibility that **16** could be capable of equilibration between argentized cyclopropyl cation **22** and cyclopropylcarbinyl cation **23**. It is very



unlikely that **22** would have a concentration advantage over **23** because of the well-recognized instability of such carbonium ions. Accordingly, structure **23** should dominate. Nevertheless, it is possible that ultimate conversion of **16** to **2** (see Scheme I) is achieved by disrotatory ring opening<sup>10</sup> of the less stable species **22** to give **17**, followed by ejection of  $\text{Ag}^+$ . Alternatively, **16** could be transformed to **2** by cyclopropylcarbinyl-homoallyl cation rearrangement of **23** and loss of silver(I) from **18**. We have not been able to distinguish between these two possibilities in all cases. The highly enhanced rearrangement rates observed for **15**<sup>8</sup> and 2,6-dimethyltricyclo[4.1.0.0<sup>2,7</sup>]heptane (**24**)<sup>1</sup> do suggest, however, that the high level of substitution at the more remote cyclopropyl center induces near-synchronous, and perhaps concerted, "double edge" bond cleavage (see **25**) with incipient charge deficiency of the



cyclopropylcarbinyl type. The base-promoted elimination reaction of mesylate **26**,<sup>11</sup> which probably occurs by way of the derived cation, attests to the mechanistic feasibility of the cyclopropylcarbinyl carbonium ion pathway.

**Mechanism of Alkylidenecyclohexene Formation.** Since alkylidenecyclohexene formation is recognized to be the result of alkyl substitution at one or both bridgehead sites, the meaningful questions relate to the causative factors which give rise to the mechanistic change-over operative under such circumstances. A specific answer to this general question may be obtained by an examination of the behavior of **3** and **8** (Scheme II). We propose that oxidative addition of  $\text{Ag}^+$  to one of the two more highly hindered edge bonds and simultaneous central bond cleavage properly accommodate ethylenecyclohexene formation. In particular, the substantial isotope effect exhibited by **9** and **10** (1.21) cannot be due to the operation of inductive contributions to a somewhat remote cationic site. Rather, the result is in keeping with a hyperconjugative effect at a highly developed electrophilic center.<sup>12</sup> Because tran-

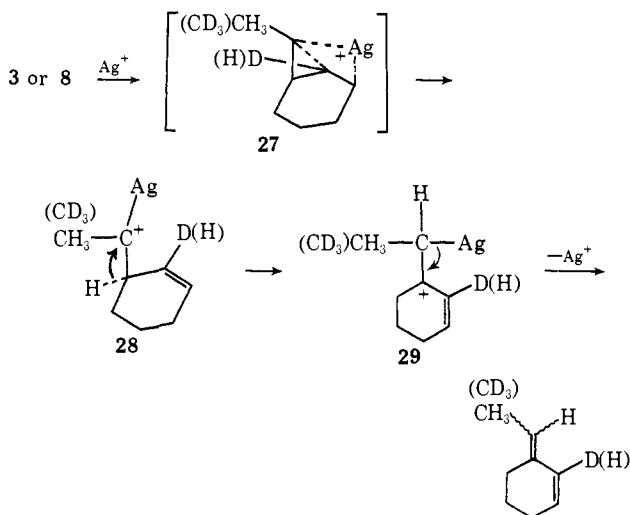
(10) S. F. Cristol, R. M. Segueira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965); P. v. R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

(11) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971).

(12) C. J. Collins and N. S. Bowman, Ed., "Isotope Effects in Chemical Reactions," Van Nostrand Reinhold Co., New York, N. Y., 1970.

(9) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963).

Scheme II

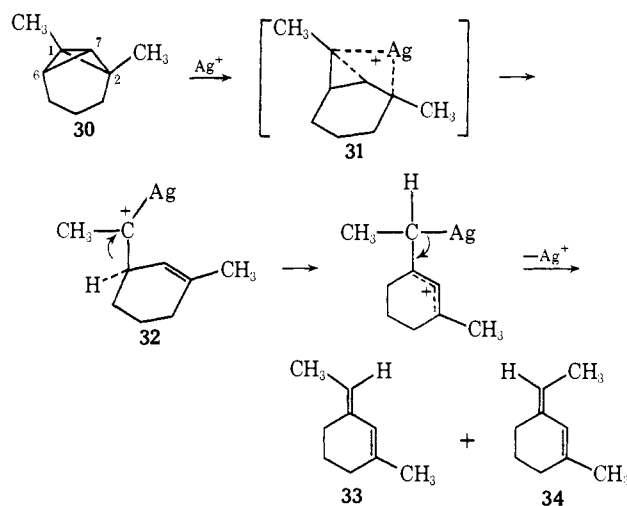


sition state **27** resembles tertiary argento carbonium ion **28**<sup>13</sup> structurally, substantial positive character should reside on the carbon bearing the  $-\text{CD}_3(\text{CH}_3)$  substituent. This mechanism bears many similarities to a reverse carbenoid addition to a double bond. The fractionation factor exhibited by **4b** and **5b** (0.95) is likewise in accord with Scheme II. Since only one deuterium is involved, the total observable impact of the effect of isotopic substitution should understandably be less than 10% per deuterium atom.

The mechanistic dichotomy resides therefore in the fact that the presence of a bridgehead alkyl group on an edge bond which is experiencing oxidative addition by  $\text{Ag}^+$  leads concomitantly to cleavage of the central bond (Scheme II) rather than subsequent rupture of a diametrically opposed edge bond (which operates when only hydrogen is present—Scheme I). The dominating factor is most plausibly the inherent stability of the argento carbonium ions in the first instance (formally tertiary). In the absence of the alkyl substituent, breakage of the central bond in an intermediate such as **16** would give rise to a less energetically favorable secondary argento carbonium ion; as a result, cyclopropyl ring opening in a different manner is here kinetically preferred.<sup>14</sup> It would appear then that the attachment of  $\text{Ag}^+$  to an  $\text{sp}^2$ -hybridized carbon atom does not provide the central atom with an overwhelming stability. Rather, our presently limited view of the situation suggests that the stability order may roughly parallel that observed with ordinary carbocations.

The regioselectivity exhibited by 1,2-dimethyltricyclo[4.1.0.0<sup>2,7</sup>]heptane (**30**) is deserving of comment. The possibility of competitive  $\text{C}_1\text{C}_2$ – $\text{C}_1\text{C}_7$  and  $\text{C}_1\text{C}_6$ – $\text{C}_1\text{C}_7$  cleavage in this hydrocarbon can be completely dismissed on the basis of the ethylidencyclohexenes formed upon rearrangement. The positioning of the methyl substituents in **33** and **34** is soundly relatable only to substantially preferred rupture of the most

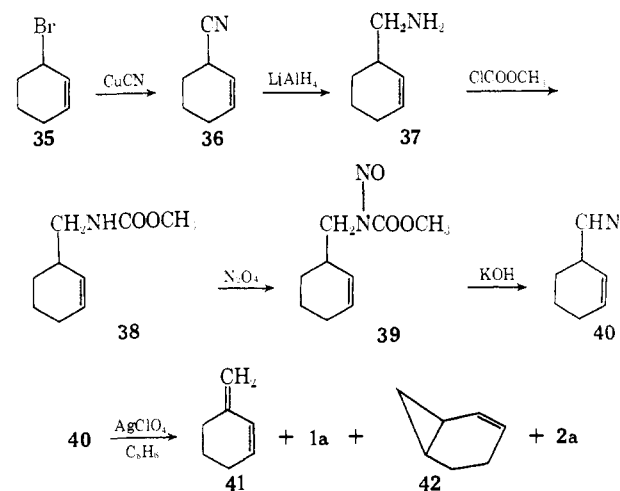
Scheme III



highly substituted edge bond ( $\text{C}_1\text{C}_2$ ; see Scheme III). It follows then that argento carbonium ion formation is appreciably accelerated by incremental alkyl substitution. This conclusion stands in contrast to that advanced earlier for 1,3-cycloheptadiene production. The difference in the latter situation relates, of course, to the inaccessibility of the alkyl group to the electron-deficient centers during the conversion to diene.

Substantial additional support for the plausibility of the argento carbonium ion hypothesis was gained from a study of the  $\text{Ag}(\text{I})$ -promoted decomposition of **40** and related diazoalkenes.<sup>8,15</sup> Consideration of the recent observations of Kirmse<sup>16</sup> and Moser<sup>17</sup> which suggests that reactions of diazoalkanes with such transition metal ions as  $\text{Ag}^+$  give rise to transient "carbene-metal complexes" led us to pursue this plausibly similar mechanistic study. We chose to generate **40** from its *N*-nitrosourethane precursor, chiefly because of the usual preference for this method.<sup>18</sup> Synthesized by the sequence outlined in Scheme IV, diazo compound **40**

Scheme IV



(13) We herein define argento carbonium ion as a cationic species in which  $\text{Ag}(\text{I})$  is bonded to an  $\text{sp}^2$ -hybridized electron pair.

(14) Recently, it has been stated that our earlier proposal<sup>8c</sup> regarding the intervention of argento carbonium ions was meant to apply to nearly all  $\text{Ag}(\text{I})$ -catalyzed reactions of bicyclobutanes [M. Sakai and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 4610 (1971)]. In actuality, we cautiously proposed at that time only "that interaction of silver(I) ion with bicyclobutanes results in rupture of two strained bonds to produce, at least in certain cases, a cationic species with  $\text{Ag}^+$  bonded to an  $\text{sp}^2$ -hybridized electron pair."

(15) Subsequent to the appearance of our initial postulate on argento carbonium ion intermediates<sup>8c</sup> and to the execution of this phase of our overall study, Sakai and Masamune published a preliminary communication describing in part a comparable investigation of diazoalkene decomposition (ref 14).

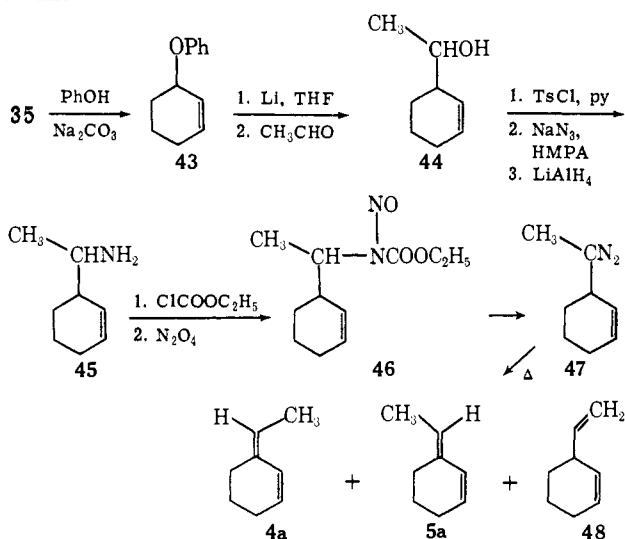
(16) W. Kirmse and K. Horn, *Chem. Ber.*, **100**, 2698 (1967).

(17) W. R. Moser, *J. Amer. Chem. Soc.*, **91**, 1135 (1969).

(18) J. March, "Advanced Organic Chemistry: Reactions, Mechanism, and Structure," McGraw-Hill, New York, N. Y., 1968, p 780.

was found to decompose readily when added to a benzene solution of silver perchlorate. Vacuum transfer of the low boiling products and vpc analysis revealed the major product (72% of volatile material) to be methylenecyclohexene (**41**). This diene invariably contained a small amount (~3%, nmr analysis) of an isomeric impurity considered to be **1a**. When such a sample of **41** was treated with  $\text{AgBF}_4$  for short periods, the six-proton singlet due to **1a** diminished and comparable quantities of 1,3-cycloheptadiene (**2a**) were produced (vpc analysis). Thus, it was evident that approximately 3% of **1a** was also formed. The remaining 25% of volatile material (seven components) was not exhaustively studied; however, two of the more significant constituents did exhibit vpc retention times identical with those of **42** (5%) and **2a** (~3%) under the conditions employed. It is not known whether the quantity of **2a** is the result of vinyl or alkyl migration in **40** (less likely) or of  $\text{Ag}^+$ -induced isomerization of additional **1a** produced in the diazo decomposition (more likely). These results strongly suggest that argento carbonium ions do indeed experience facile 1,2-hydride shift (when possible) and that 1,3-cycloheptadienes do not arise in a major way from such intermediates.

Attempts to expose **47** (Scheme V) to silver ion in Scheme V



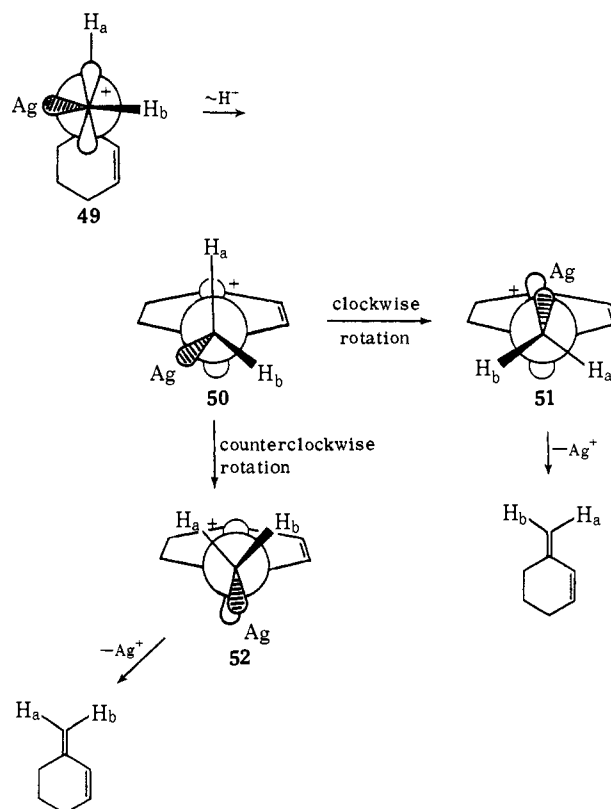
order to compare the reactivities of secondary and tertiary argento carbonium ions were not successful. Although **47** could be synthesized, the rate at which nitrogen was lost from this diazo compound under conditions of its formation was too great to permit admixture with solutions of  $\text{Ag(I)}$  salts. Nevertheless, the uncatalyzed thermal behavior of the desired carbene is reflected in the products, which consisted of **4a** (33%), **5a** (33%), and **48** (23%). Diene **48** was prepared independently by the coupling reaction of vinylmagnesium chloride and 3-bromocyclohexene; its nmr features also correspond to the previously reported values.<sup>19</sup> Thus, 1,2-hydride shifts account again for the major proportion (at least 90%) of the products with the remainder consisting of four unidentified hydrocarbons.<sup>20</sup>

Existing theoretical calculations pertaining to hydrogen migration in ethylidene do not permit differ-

(19) N. F. Cywinski, *J. Org. Chem.*, **30**, 361 (1965).

(20) The behavior of 3-cyclohexenylcarbinylcarbene (as generated from the tosylhydrazone) has also been investigated: H. Babad, W. Flemon, and J. B. Wood, III, *J. Org. Chem.*, **32**, 2871 (1967).

entiation between rearrangement to the filled or unfilled orbital.<sup>21</sup> However, the recently established parallelism between migratory aptitudes to carbonium<sup>22</sup> and carbenoid centers<sup>23</sup> is most consistent with stereo-electronically controlled shifts to the unfilled orbital on the  $\text{sp}^2$ -hybridized carbon in the two systems. Accordingly, we assign analogous behavior to argento carbonium ions. Using the 2-cyclohexenylcarbinyl argento carbonium ion (**49**) as a model (only one rotamer shown), we note that the 1,2-hydride shift from this conformer generates an allylic cation **50** which neces-



sarily must experience C-C bond rotation before loss of  $\text{Ag}^+$  can materialize. Since both clockwise and counterclockwise rotation to give **51** and **52**, respectively, is possible, the ultimate stereochemistry of the alkylidene-cyclohexene is dictated by the usual factors which affect such eliminations.

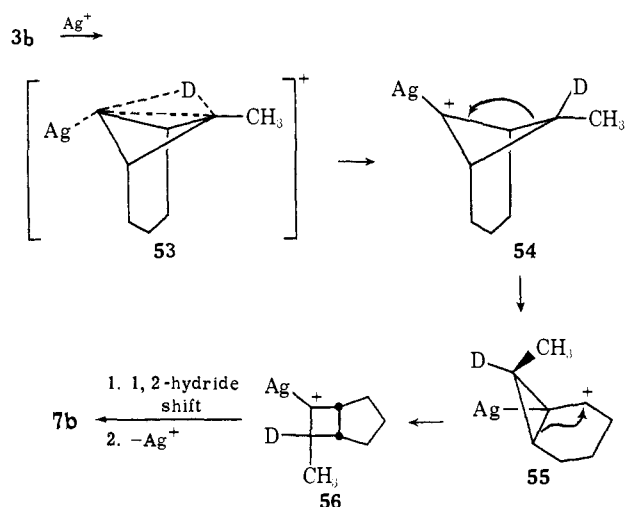
**The Rearrangement to Bicycloheptenes.** The magnitude of the primary effect isotope effect experienced by **7** (1.74) would seem to suggest that the bridgehead C-H or C-D bond is rather extensively affected at the transition state. In view of the very small fractionation factor shown by **12** (1.03), the carbon atom bearing the methyl group clearly does not assume any significant degree of positive charge in the rate-determining step. Initially, the 1,3-hydride shift mechanism outlined in Scheme VI was suggested to explain these observations.<sup>5</sup> However, because the mechanism outlined in Scheme VI is a rather circuitous one made to conform to the isotope effect data, we immediately questioned whether the magnitude of the  $k_{\text{H}}/k_{\text{D}}$  value in this instance was

(21) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968); see also R. Hoffmann, R. Gleiter, and F. B. Mallory, *ibid.*, **92**, 1460 (1970).

(22) Y. E. Rhodes and T. Takino, *ibid.*, **92**, 5270 (1970), and references therein.

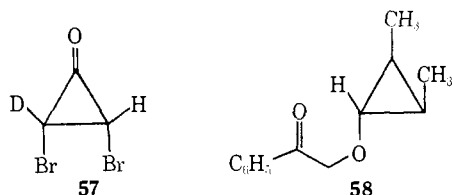
(23) A. R. Kraska, L. I. Cherney, C. G. Moseley, G. M. Kaufman, and H. Shechter, manuscript in preparation.

## Scheme VI



truly serving as an accurate index of a rate-limiting hydride transfer operative at the transition state. In fact, the continuing theoretical debate<sup>12,24</sup> over those precise parameters which can affect the kinetic isotope effect was sufficient to engender a number of reservations as to the applicability of the original considerations of Westheimer<sup>25</sup> and Bigeleisen<sup>26</sup> to the present situation where strained rings are involved.

In this regard, two other recent developments lend credence to the contention that small ring compounds can generate surprisingly large secondary deuterium isotope effects. Thus, Rappe and Knutson have established that the cleavage of monodeuteriodibromocyclopropanone (**57**) with aqueous bases operates with a  $k_{\text{H}}/k_{\text{D}}$  of 1.6–1.7 and attributed the magnitude of this fractionation factor to "the conditions encountered in the cyclopropanone ring system."<sup>27</sup> Also, Darling and Turro have studied the photorearrangement of **58** to its



all-cis and -trans epimers;<sup>28</sup> when the  $\gamma$  hydrogen of **58** is replaced by deuterium, an isotope effect of 2.5 results. Since carbonyl- $\gamma$ -hydrogen interaction does operate in the traditional type II manner, these workers concluded that isomerization of the back C–C bond is coupled with stretching (but not total cleavage) of the  $\gamma$ -H–C bond.

Accordingly, these data suggest that the tricycloheptane–bicycloheptene rearrangement need not re-

(24) Consult, for example: (a) A. V. Willi and M. Wolfsberg, *Chem. Ind. (London)*, 2097 (1964); (b) R. F. W. Bader, *Can. J. Chem.*, **42**, 1822 (1964); (c) R. P. Bell, *Discuss. Faraday Soc.*, **39**, 16 (1965); (d) W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **91**, 16 (1969); (e) R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967); (f) F. G. Bordwell and W. J. Boyle, Jr., *J. Amer. Chem. Soc.*, **93**, 512 (1971); (g) H. Kwart and M. C. Latimore, *ibid.*, **93**, 3770 (1971).

(25) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961); see also K. B. Wiberg, *ibid.*, **55**, 713 (1955).

(26) J. Bigeleisen, *Pure Appl. Chem.*, **8**, 217 (1964).

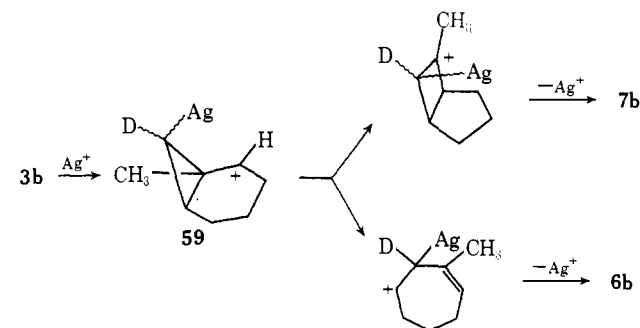
(27) C. Rappe and L. Knutson, *Angew. Chem., Int. Ed. Engl.*, **11**, 329 (1972).

(28) T. R. Darling and N. J. Turro, *J. Amer. Chem. Soc.*, **94**, 4366 (1972). We thank Professor Turro for informing us of his results prior to publication.

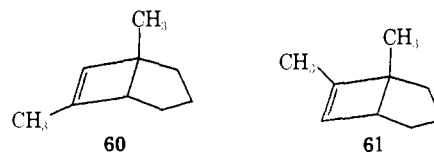
quire actual scission of the bridgehead C–H bond. Studies presently in progress in this laboratory also support this conclusion.

Gassman and Atkins<sup>29</sup> have proposed instead the bond reorganization pathway outlined in Scheme VII

## Scheme VII

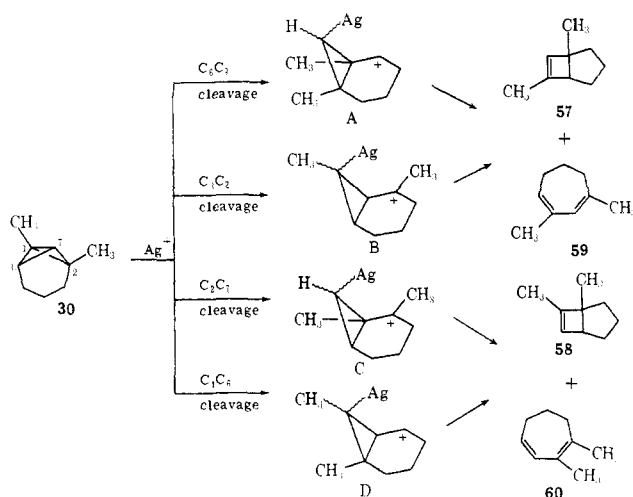


in which intermediate **59** serves as the precursor to both bicycloheptene and cycloheptadiene products. Although the isotope data clearly discount the possibility of a common rate-determining step in these two reactions, an additional disclaimer to this proposal comes from knowledge of the behavior of **30** under conditions of Ag(I) catalysis.<sup>1</sup> It will be recalled that the major product of this rearrangement (52% yield) is bicycloheptene **60**. No other bicycloheptene of differing



methyl substitution, particularly **61**, was found.<sup>1</sup> Consequently, were the Gassman mechanism operative, **30** would be required to exhibit a strong preference for initial  $\text{C}_1\text{C}_2$  or  $\text{C}_6\text{C}_7$  bond cleavage, since oxidative addition by  $\text{Ag}^+$  into the remaining edge bonds would eventually afford some **61** (Scheme VIII). Because earlier

## Scheme VIII



observations have demonstrated that  $\text{C}_2$  methyl groups promote attack of  $\text{Ag}^+$  at an adjacent edge bond, the  $\text{C}_1\text{C}_2$  process should be favored. But these conclusions suffer from at least two disadvantages. Firstly, neither reaction pathway provides access to 1,2-di-

(29) P. G. Gassman and T. J. Atkins, *ibid.*, **93**, 4597 (1971).

dimethyl-1,3-cycloheptadiene (**63**), the major diene produced in the rearrangement.<sup>1,30</sup> Secondly, numerous experiments are now available<sup>1,8</sup> to support the proposition that intermediate **A** should give rise virtually exclusively to **62** (Scheme I), whereas intermediate **B** should eventuate in alkenylidencyclohexene formation (Scheme II).<sup>31</sup>

We do not yet know the causative factor underlying the large isotope effect. Our present data do allow certain of the more obvious pathways to be discounted, but additional work of both a kinetic and structural nature is required for ultimate solution of this question.

**Effect of Catalyst Variation.** The molecular changes involved in the transition metal catalyzed rearrangement of bicyclo[1.1.0]butanes are markedly dependent upon the nature of the catalyst. For example, treatment of **1a** with catalytic quantities of rhodium dicarbonyl chloride dimer,<sup>32</sup> bisbenzotrileidichloropalladium,<sup>33</sup> related palladium catalysts,<sup>29</sup> iridium tricarbonyl chloride dimer,<sup>29</sup> or pentafluorophenylcopper tetramer<sup>29</sup> results in isomerization exclusively to 3-methylenecyclohexene (**40**). 1-Methyltricyclo[4.1.0.0<sup>2,7</sup>]heptane (**3a**) exhibits analogous behavior and affords **64**.<sup>29</sup> Exposure of **1a** to the action of anhydrous magnesium bromide<sup>34,35</sup> or stannous chloride dihydrate<sup>29</sup> on the other hand gives rise only to norcarene (**42**), whereas the effect of platinum oxide, ruthenium tricarbonyl dichloride dimer, and bis(triphenylphosphine)rhodium carbonyl chloride is to partition product distribution between **41** (major) and **42** (Scheme IX).<sup>29</sup>

The dramatic product crossover encountered with the group b catalysts could conceivably arise because of a substantially enhanced driving force to produce the so-called "metal complexed carbene-metal bonded carbonium ion hybrid" **66**.<sup>36</sup> Preceding discussion has made reference to the fact that the generation of argento carbonium ions appears dictated chiefly by the extent of substitution at the incipient cationic center, with only tertiary systems gaining apparent mechanistic significance. In contrast, rhodium, palladium, and iridium catalysts seemingly do not suffer from this dependency, a likely consequence of the combined polarizability and  $\sigma$  donor- $\pi$  acceptor ability of the ligands in such complexes. With the  $\sigma$  electron acceptor ability of the catalyst also contributing to the outcome of the rearrangement, intermediates of type **66** intervene irrespective of the number of alkyl groups attached to the electron-deficient center. 1,2-Hydride shift and ejection of metal complete the conversion to the alkenylidencyclohexenes.

The role played by Mg(II) and Sn(II) salts remains to be elucidated. Masamune has proposed that metallo

(30) We point out that the observed ratio of **63** to **62** (85:15) corresponds fully to the expected differences in initial cleavage rates of the C<sub>2</sub>C<sub>7</sub> and C<sub>6</sub>C<sub>7</sub> bonds (ref 1). It is our present contention that these two pathways operate competitively with those leading to the other products.

(31) The much less plausible possibility exists that the four bond cleavages in Scheme VIII operate concurrently, but with high levels of stereoselectivity in each instance.

(32) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 1042 (1971).

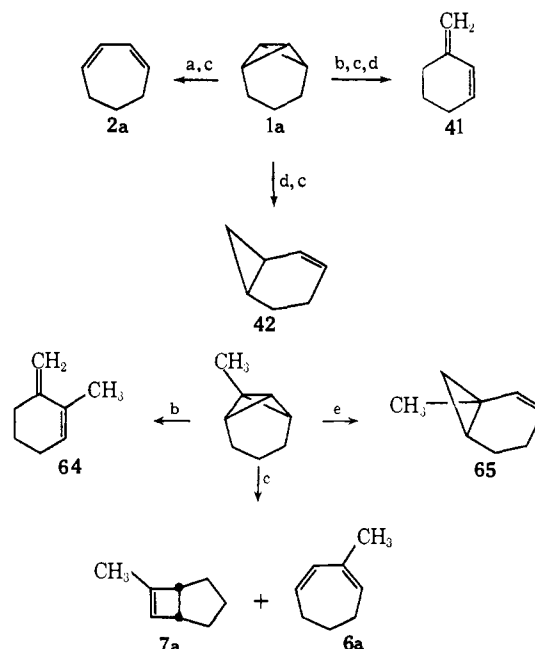
(33) M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Commun.*, 486 (1971).

(34) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

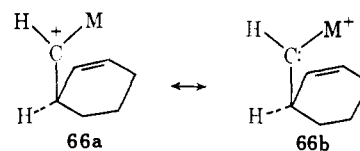
(35) L. A. Paquette and S. E. Wilson, *J. Org. Chem.*, in press.

(36) P. G. Gassman, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1812 (1971).

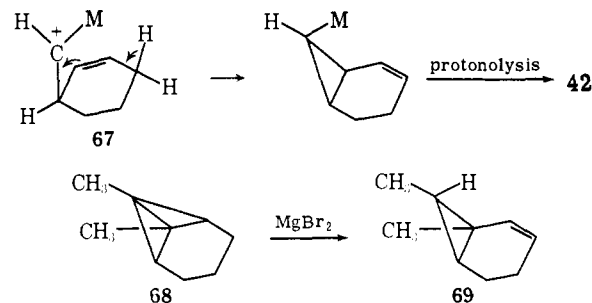
Scheme IX



<sup>a</sup> Ag<sup>+</sup>. <sup>b</sup> [Rh(CO)<sub>2</sub>Cl]<sub>2</sub>, Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>Cl<sub>2</sub>, [Ir(CO)<sub>3</sub>Cl]<sub>2</sub>, [( $\pi$ -allyl)-PdCl]<sub>2</sub>, (C<sub>6</sub>F<sub>5</sub>Cu)<sub>4</sub>. <sup>c</sup> ZnI<sub>2</sub>, HgBr<sub>2</sub>. <sup>d</sup> [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Rh(CO)Cl, [Ru(CO)<sub>3</sub>Cl]<sub>2</sub>, PtO<sub>2</sub>. <sup>e</sup> MgBr<sub>2</sub>, SnCl<sub>2</sub>·2H<sub>2</sub>O.



carbonium ions such as **67** serve also as precursors of



the vinylcyclopropane type products.<sup>11</sup> Whatever the precise mechanism, the high levels of stereoselectivity encountered in such reactions, as exemplified by the behavior of **68**,<sup>35</sup> must be adequately accounted for.

## Experimental Section

Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer and apparent coupling constants are cited. Elemental analyses were performed by the Scandinavian Micro-analytical Laboratory, Herlev, Denmark.

**Determination of the Isotope Effect for 1b.** 1,7-Dideuteriotricyclo[4.1.0.0<sup>2,7</sup>]heptane (**1b**) was treated with  $8.45 \times 10^{-2}$  M silver perchlorate in benzene (freshly titrated) at 40.00° exactly in the manner prescribed for **1a**.<sup>1</sup> The same vpc response factors were employed and the following second-order rate constants were measured:  $2.67 \times 10^{-3}$ ,  $2.68 \times 10^{-3}$ ,  $2.68 \times 10^{-3}$ ,  $2.69 \times 10^{-3}$ , and  $2.66 \times 10^{-3}$  l./mol sec. An average value of  $2.68 \pm 0.01 \times 10^{-3}$  l./mol sec was calculated from these five runs. The inverse isotope effect,  $k_H/k_D = 0.847$ , was readily extracted from these data.

**1-Trideuteriomethyltricyclo[4.1.0.0<sup>2,7</sup>]heptane (8).** Under a nitrogen atmosphere, 2.0 g (17 mmol) of tetramethylethylenediamine (TMEDA) was added to 13 ml (16 mmol) of cold 1.2 M *n*-butyllithium in pentane. This was followed by the addition of 1.5 g (16

mmol) of **1a**. The mixture was heated to reflux for 2 hr, during which time a light yellow solid appeared, and then cooled in ice. Trideuteriomethyl iodide (2.9 g, 20 mmol) in 5 ml of pentane was added dropwise during 15 min and an exothermic reaction ensued. Water (10 ml) was slowly introduced, followed by 50 ml of pentane. The resulting organic phase was washed with saturated aqueous cupric sulfate solution to remove residual TMEDA. After drying, the solution was concentrated by careful distillation through a short Vigreux column. The remaining material was distilled at 15 mm and 70° and collected in a Dry Ice-acetone trap. Ultimate purification of **8** was achieved by sequential preparative scale vpc separation on a 1/4 in. × 10 ft column packed with 5% OV-17 at 100° and a 10% SE-30 column of similar dimensions at 90°: yield 400 mg;  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  2.12–2.33 (m, 2), 1.28 (pseudosinglet, 6), and 1.02 (t,  $J = 3$  Hz, 1).

**Determination of the Isotope Effects for 3b and 8.** The vpc response factors for **3a–7a** were determined relative to mesitylene which was employed as the internal standard. A 1/4 in. × 10 ft 5% OV-17 column maintained at 85° was employed in these experiments. Plots of the molar ratios of mesitylene to each of the hydrocarbons *vs.* the peak-area ratios of these isomers were linear in each instance. The inverse of the slopes of these plots gave the desired response factors: **3** (1.22), **4** and **5** (1.19), **6** (1.10), and **7** (1.33). Two runs with **3a** confirmed a 96% conversion to products during 3 hr at 40.00° in  $8.45 \times 10^{-2}$  M silver perchlorate-benzene.

The isotope effects were determined by vpc analysis of the product distributions after exactly 300 sec (corresponding to *ca.* 9% reaction) as previously described.<sup>1</sup> Five separate runs were conducted for **3a**, **3b**, and **8**. The various fractionation factors then followed from simple division of the product compositions. Because **3** and **7** possess approximately the same retention times on the OV-17 column, the peak area of **7** was not determined until the end of the reaction. The computations associated with the isomerization of **3b** are given as illustrative of the procedure employed (mes = mesitylene): (**4a** + **5a**<sub>area</sub>)/mes<sub>area</sub> =  $0.271 \pm 0.004$  (at ~9% reaction); (**4b** + **5b**<sub>area</sub>)/mes<sub>area</sub> =  $0.286 \pm 0.004$ ; **6a**<sub>area</sub>/mes<sub>area</sub> =  $0.263 \pm 0.004$  (at ~9% reaction); **6b**<sub>area</sub>/mes<sub>area</sub> =  $0.288 \pm 0.004$ ; **7a**<sub>area</sub>/**6a**<sub>area</sub> =  $1.39 \pm 0.01$  (at 100% reaction); **7b**<sub>area</sub>/**6b**<sub>area</sub> =  $0.726 \pm 0.012$ . The isotope effects now follow from these experimentally derived ratios

$$\frac{\mathbf{6a}_{\text{area}}/\text{mes}_{\text{area}}}{\mathbf{6b}_{\text{area}}/\text{mes}_{\text{area}}} = \frac{\mathbf{6a}_{\text{area}}}{\mathbf{6b}_{\text{area}}} = \frac{0.263 \pm 0.004}{0.288 \pm 0.004} = 0.913$$

$$\frac{\mathbf{4a} + \mathbf{5a}_{\text{area}}/\text{mes}_{\text{area}}}{\mathbf{4b} + \mathbf{5b}_{\text{area}}/\text{mes}_{\text{area}}} = \frac{\mathbf{4a} + \mathbf{5a}_{\text{area}}}{\mathbf{4b} + \mathbf{5b}_{\text{area}}} = \frac{0.271 \pm 0.004}{0.286 \pm 0.004} = 0.948$$

$$\frac{\mathbf{7a}_{\text{area}}/\mathbf{6a}_{\text{area}}}{\mathbf{7b}_{\text{area}}/\mathbf{6b}_{\text{area}}} = \frac{\mathbf{7a}_{\text{area}}}{\mathbf{7b}_{\text{area}}} = \frac{1.39 \pm 0.01}{0.726 \pm 0.012} \times 0.913 = 1.74$$

The ratio of **4b**:**5b**, analyzed on a 1/4 in. × 20 ft 5% QF-1 column, showed the ratio (4:1) to be unchanged from that observed in the protio series.

In the case of **3b**, the various products were characterized additionally by nmr analysis (CDCl<sub>3</sub> solution,  $\delta$  values). Due to the availability of limited quantities, this was not done in the studies with **8**: for **4b–5b**, 5.53–5.87 (m, 1), 5.20 (m, 1), and 1.52–2.51 (m, 9); for **6b**, 5.72 (m, 2), 1.6–2.5 (m, 6), and 1.78 (m, 3); for **7b**, 2.88–3.17 (m, 2), 0.87–1.84 (m, 6), and 1.60 (s, 3).

To confirm the position of the deuterium in **6b**, a small sample was photoisomerized (quartz tube, 450-W Hanovia lamp, 1.5 hr) in ether. The sole product was identical by nmr with **7b**.

**3-Cyanocyclohexene (36).**<sup>37</sup> An intimate mixture of 32.20 g (0.20 mol) of 3-bromocyclohexene and 18.80 g (0.21 mol) of cuprous cyanide was stirred mechanically at room temperature for 19 hr. At the end of this time, the flask was heated to 100° for 45 min. A distillation head was fitted to the flask and the product was dis-

tilled directly to give 12.01 g (56%) of **36**: bp 80–85° (15 mm) [lit.<sup>38</sup> bp 88–89° (17 mm)];  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  5.45–6.15 (m, 2, olefinic), 3.1–3.4 (br s, 1, >CHCN), 1.4–2.3 (m, 6, remaining methylenes).

**(2-Cyclohexenyl)methylamine (37).** A solution of 19.89 g (0.186 mol) of **36** in 75 ml of anhydrous ether was added dropwise during 1 hr to a refluxing slurry of 10.6 g (0.279 mol) of lithium aluminum hydride in 425 ml of the same solvent. This mixture was heated at reflux for 12 hr, cooled in ice, and treated sequentially with water (10 ml), 30% KOH solution (10 ml), water (30 ml), and anhydrous magnesium sulfate. The salts were removed by filtration and washed well with ether. Evaporation of the combined filtrates and distillation gave 12.48 g (60.5%) of **37**: bp 69–72° (22 mm) [lit.<sup>39</sup> bp 75–80° (20 mm)];  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  5.68 (m, 2, olefinic), 2.62 (br d, 2, CH<sub>2</sub>N<), and 1.0–2.4 (m, 9). The picrate of **37** was obtained as yellow crystals, mp 141.5–143°, from ethanol (lit.<sup>39</sup> mp 130–132°).

**Methyl N-(2-Cyclohexenylmethyl)carbamate (38).** To 5.24 g (0.0472 mol) of **37** dissolved in an ice-cold mixture of 50 ml of ether and 20 ml of water was added half of a solution of 4.48 g (0.474 mol) of methyl chloroformate in 10 ml of ether. With stirring, the remaining half of this solution was then added simultaneously with a solution of 1.90 g (0.0745 mol) of sodium hydroxide in 30 ml of water. After 1 hr, additional ether was added and the organic layer was washed with sodium chloride solution, dried, and evaporated. A quantitative yield of pure viscous oil was obtained, an analytical sample of which was prepared by molecular distillation at 50° (0.8 mm):  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  4.9–6.0 (m, 3, olefinic and >NH), 3.62 (s, 3, OCH<sub>3</sub>), 3.12 (t,  $J = 6.5$  Hz, 2, CH<sub>2</sub>NH), and 1.0–2.6 (m, 7).

Anal. Calcd for C<sub>9</sub>H<sub>15</sub>NO<sub>2</sub>: C, 63.88; H, 8.94; N, 8.28. Found: C, 64.02; H, 9.09; N, 8.28.

**Methyl N-Nitroso-N-(2-cyclohexenylmethyl)carbamate (39).**<sup>40</sup> A slurry of 7.87 g (0.0465 mol) of **38** and 7.6 g (0.093 mol) of sodium acetate in 65 ml of glacial acetic acid was cooled almost to the point of solidification and purged with a stream of nitrogen. Dinitrogen tetroxide (2.85 ml, 0.0465 mol) was introduced *via* syringe, stirring was continued for *ca.* 45 min, and the mixture was poured into ether and water. The organic layer was washed well with water, sodium bicarbonate, and sodium chloride solutions, dried, and evaporated. The nmr spectrum of the bright yellow liquid (7.73 g) indicated the presence of ~20% unreacted **38** and therefore the mixture was recycled with 0.7 ml of dinitrogen tetroxide, 3.6 g of sodium acetate, and 50 ml of glacial acetic acid. Work-up gave 7.48 g (81%) of bright yellow liquid showing no impurities in the nmr spectrum. An analytical sample was prepared by molecular distillation at 40–50° (0.04 mm):  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  5.18–5.92 (m, 2, olefinic), 4.03 (s, 3, OCH<sub>3</sub>), 3.68 (d, 2, CH<sub>2</sub>N<), and 1.0–2.5 (m, 7).

Anal. Calcd for C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 54.53; H, 7.12; N, 14.13. Found: C, 54.74; H, 7.18; N, 14.21.

**2-Cyclohexenyldiazomethane (40).** Formation and Decomposition. To a stirred slurry of 15 ml of benzene and 10 g of potassium hydroxide in 10 ml of water cooled in ice was added a solution of **39** (2.00 g, 0.0101 mol) in 5 ml of benzene during 2 min. Stirring was continued in the dark for 15 min, at which time the mixture was poured into a precooled separatory funnel and washed with distilled water. The aqueous extracts were extracted once with a small amount of benzene and the combined benzene layers were dried over KOH pellets at 0°. This bright orange solution was added dropwise to 5.0 ml of 0.202 M silver perchlorate in benzene (~10 mol %) at 40° and nitrogen evolution was monitored with a gas buret. The observed evolution of nitrogen was 135 ml or 60% of theory. The benzene solution was washed twice with water and once with saturated sodium chloride solution. The solvent and volatile products were vacuum transferred and subjected to vpc analysis on a 1/4 in. × 24 ft 5% SF-96 on Chromosorb G column at 85°. The product composition is discussed in the text. The residue remaining after removal of the volatile products consisted of 430 mg of recovered **39**. After concentration of the distillate by removal of benzene through a Teflon-coated spinning band column, the major component was isolated by preparative scale vpc (1/4 in. × 12 ft 15% squalene on Chromosorb W at 70°) and identified as 3-methylenecyclohexene by spectral comparison with an authentic sample prepared from 2-cyclohexenone and methylenetriphenylphosphorane.

(38) M. Mousseron, F. Winternitz, J. Jullien, and R. Jacquier, *Bull. Soc. Chim. Fr.*, 79 (1948).

(39) French Patent 1,161,397 (Aug 28, 1958); *Chem. Abstr.*, 54, 18326i (1960).

(40) Adapted from the procedure of E. White, *Org. Syn.*, 47, 44 (1967).

(37) Adapted from the procedure of J. V. Supniewski and P. L. Salzberg, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 46.



**3-Phenoxy-cyclohexene (43).**<sup>41</sup> A mixture of 32.3 g (0.20 mol) of 3-bromocyclohexene, 18.8 g (0.20 mol) of phenol, and 27.8 g (0.20 mol) of potassium carbonate in 200 ml of acetone was refluxed for 51 hr. After evaporation of the solvent, water and ether were added and the organic layer was washed with 10% sodium hydroxide and saturated sodium chloride solutions and dried. Distillation of the product afforded 25.45 g (73%) of **43**: bp 71–73° (0.25 mm);  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  6.57–7.42 (m, 5, aromatic), 5.72 (br, 2, olefinic), 4.7 (m, 1, >CHO), and 1.2–2.2 (m, 6).

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{14}\text{O}$ : C, 82.72; H, 8.10. Found: C, 82.60; H, 8.04.

**1-(2-Cyclohexenyl)ethanol (44).** Lithium ribbon (11.1 g, 1.6 g-atom) was weighed into a 1-l. three-necked flask containing 400 ml of anhydrous tetrahydrofuran. A small portion of a solution of 69.8 g (0.40 mol) of **43** in 50 ml of dry ether was added in addition to a spatula of biphenyl. The mixture was stirred mechanically at room temperature under 1 atm of nitrogen until the reaction began as evidenced by the development of a deep red color. The mixture was cooled to  $-25^\circ$  and the remainder of **43** was added dropwise. After completion of the addition, the red-brown mixture was stirred for 1 hr at  $-40$  to  $-45^\circ$ . Acetaldehyde (26 ml) was slowly introduced and stirring was maintained for 6 hr at the same low temperatures. The mixture was allowed to warm to room temperature and filtered through a glass wool plug to remove unreacted lithium. Ether and water were added and the resulting water layer was extracted three times with ether. Customary processing of the combined organic layers afforded 22.3 g (44%) of **44**, bp 61–67.5° (1.7 mm), together with 18.6 g of recovered **43**. An analytical sample of **44** was prepared by vpc purification on a  $\frac{1}{4}$  in.  $\times$  20 ft 5% QF-1 on Chromosorb G column:  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  5.38–6.0 (m, 2, olefinic), 3.67 (symmetrical six-line pattern, 1, >CHOH), 1.0–2.7 (m, 8, ring protons and OH), and 1.15 (d,  $J = 6$  Hz,  $\text{CH}_3$ ).

*Anal.* Calcd for  $\text{C}_8\text{H}_{14}\text{O}$ : C, 76.14; H, 11.18. Found: C, 76.25; H, 11.04.

**1-(2-Cyclohexenyl)ethylamine (45).** A solution of 22.30 g (0.177 mol) of **44** and 67.5 g (0.354 mol) of recrystallized *p*-toluenesulfonyl chloride and sufficient pyridine to total 500 ml was prepared at  $0^\circ$  and stored at this temperature for 65 hr. The usual work-up gave 39.10 g of the derived tosylate, mp 50.5–52.0° (from pentane), which proved somewhat unstable on standing.

A mixture of 38.10 g (0.176 mol) of this tosylate and 12.6 g (0.194 mol) of sodium azide in 300 ml of distilled hexamethylphosphoramide was heated at 60–65° with stirring under 1 atm of nitrogen for 10.5 hr. After cooling, water (500 ml) was added and the mixture was extracted several times with pentane. The pentane extracts were washed with water, saturated sodium bicarbonate, and sodium chloride solutions, cooled to  $-78^\circ$  to precipitate a white solid, and filtered, and the solvent was distilled through a small Vigreux column. There remained 17.43 g of azide which was not further purified because of suspected instability:  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  5.4–6.0 (m, 2, olefinic), 3.37 (six-line m, 1, >CHN<sub>3</sub>), 1.0–2.5 (m, 7), and 1.22 (d,  $J = 6$  Hz,  $\text{CH}_3$ ).

(41) Adapted from the procedure of C. F. H. Allen and J. W. Gates, Jr., "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 140.

To a slurry of 6.65 g of lithium aluminum hydride in 450 ml of dry ether was added dropwise during 15 min a solution of 20.67 g of crude azide in 50 ml of ether. The solution was refluxed for 11 hr and processed in the customary alkaline fashion to give 8.00 g of **45**: picrate mp 182–184° dec (from ethanol);  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  5.4–6.0 (m, 2, olefinic), 2.85 (m, 1 >CHN<), 0.9–2.3 (m, 12).

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_7$ : C, 47.45; H, 5.12; N, 15.81. Found: C, 47.37; H, 5.21; N, 15.85.

**1-(2-Cyclohexenyl)diazoethane (47).** Synthesis and Decomposition. Carbamate was prepared from 7.80 g (0.062 mol) of **45**, 6.80 g (0.063 mol) of ethyl chloroformate, and 2.50 g (0.063 mol) of sodium hydroxide as previously described: yield, 11.51 g (93.5%). The analytical sample was prepared by molecular distillation at  $40^\circ$  (0.05 mm).

*Anal.* Calcd for  $\text{C}_{11}\text{H}_{19}\text{NO}_2$ : C, 66.97; H, 9.71; N, 7.10. Found: C, 67.22; H, 9.75; N, 7.16.

In the predescribed fashion, 2.09 g (10.6 mmol) of the carbamate was treated with 0.65 ml (10.6 mmol) of dinitrogen tetroxide and 1.74 g (21.0 mmol) of sodium acetate in 16 ml of glacial acetic acid. The yield of the derived *N*-nitrosocarbamate (**46**) was 2.06 g (86%).

To a cooled (ice-bath) stirred suspension of 5 ml of 50% KOH solution, 10 ml of benzene, and 5 ml of Carbitol was added 1.00 g (4.45 mmol) of **46** dissolved in 3 ml of benzene. Gas evolution was monitored with a gas buret. After 30 min, 75 ml (75%) of nitrogen had been evolved. No additional gas evolution was evidenced during an additional 2-hr period. Work-up as before and product analysis on the 5% QF-1 column at  $72^\circ$  indicated the presence of three major components identified as **4a** (33%), **5a** (33%), and **48** (23%). The several minor components were not identified. The 3-vinylcyclohexane (**48**) isolated from this study was identical with the authentic sample prepared as described below.

**3-Vinylcyclohexene (48).** Into a 100-ml three-necked flask fitted with a Dry Ice condenser, gas inlet tube, thermometer, and magnetic stirrer was placed 2.43 g (0.10 g-atom) of magnesium turnings and 40 ml of anhydrous tetrahydrofuran. A crystal of iodine and a few drops of ethylene dibromide were added and vinyl chloride was introduced below the surface of the solvent. The introduction of the gas was repeated at intervals until most of the metal had been consumed. A solution of 16.10 g (0.10 mol) of **35** in 15 ml of dry ether was added at a rate sufficient to maintain gentle reflux. After stirring for 2 hr at room temperature, the mixture was poured onto ice and water and the aqueous phase was extracted with ether. The combined organic layers were washed with saturated sodium bicarbonate and sodium chloride solutions, dried, and concentrated. Distillation of the residue furnished 2.32 g of colorless liquid, bp 75–85° (140 mm), which contained approximately 75% of **48** (vpc analysis). A pure sample of **48** was obtained by preparative vpc isolation ( $\frac{1}{4}$  in.  $\times$  20 ft 5% QF-1 on Chromosorb G column at  $90^\circ$ ). Its spectral properties were consistent with those reported in the literature.<sup>19</sup>

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