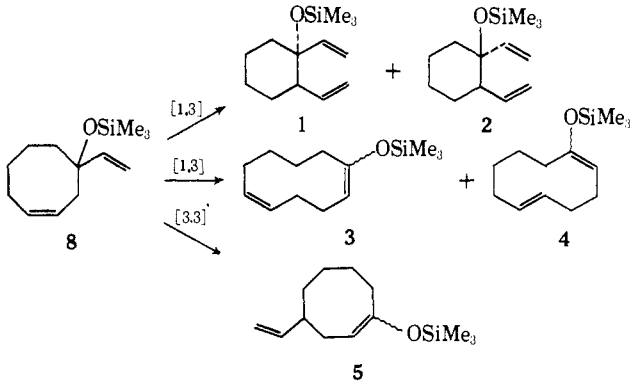
Thermal Rearrangements of *cis*- and *trans*-1-Trimethylsiloxy-1-vinylcyclodec-3-ene. Ring Strain Effects for the Siloxy-Cope Rearrangement[1]

Richard W. Thies* and J. E. Billigmeier

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received July 23, 1973*

Abstract: Thermal rearrangement of *cis*- or *trans*-1-trimethylsiloxy-1-vinylcyclodec-3-ene gives predominantly the [1,3] shift ring expansion product, *cis*-cyclododec-5-en-1-one, in which the stereochemistry of the ring double bond is maintained. The minor products, *trans*-cyclododec-5-en-1-one and 4-vinylcyclodecanone, correspond to a [1,3] shift ring expansion with loss of double bond stereochemistry and to a [3,3] sigmatropic shift. The ring double bond is shown to be vital to the reaction. The activation parameters for various ring sizes correlate to some extent with strain energy but also with the estimated overall energetics of the reaction.

Previous papers in this series[2,3] have described the rearrangements of *cis*-1-trimethylsiloxy-1-vinylcyclooct-3-ene (**8**) and the nine-membered ring analog, **9**. For **8**, the major rearrangement pathways are



[1,3] sigmatropic shift ring contraction (**1** and **2**) and [1,3] shift ring expansion (**3**). The minor products represent [1,3] shift ring expansion with geometric isomerization of the ring double bond (**4**) and [3,3] sigmatropic shift (**5**). The rearrangements that generate enol forms (**3**, **4**, and **5**) have been termed siloxy-Cope rearrangements by analogy with the oxy-Cope terminology.[4] Formation of such enol forms provides a substantial driving force for the siloxy-Cope reactions; however, for **8** ring-strain changes favor the nonenol forms **1** and **2** to the extent that both types of products are observed.[2] The change in ring strain associated with ring contraction is less favorable for the nine-membered ring case, **9**, and for that system only products analogous to **3**, **4**, and **5** are observed.[3]

The present work reports the cis and trans ten-membered analogs **10c** and **10t** which probe the question of geometric isomerization of the double bond, the importance of ring strain to the rearrangement, and the generality of the rearrangement.

(1) Portions of this work have been presented previously: (a) R. W. Thies and J. E. Billigmeier, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., 1971, Abstract No. 162; (b) R. W. Thies, M. T. Wills, J. E. Billigmeier, and R. Bolesta, 28th Annual Northwest Regional Meeting of the American Chemical Society, Pullman, Wash., 1973, Abstract No. 0.11.

(2) R. W. Thies, M. T. Wills, A. W. Chin, L. E. Schick, and E. S. Walton, *J. Amer. Chem. Soc.*, **95**, 5281 (1973).

(3) R. W. Thies, *ibid.*, **94**, 7074 (1972); *Chem. Commun.*, 237 (1971).

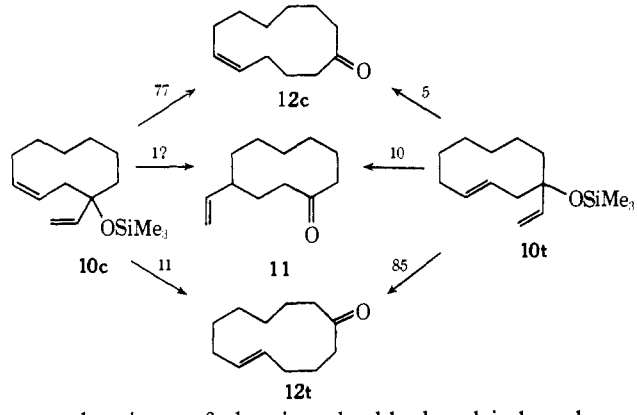
(4) J. A. Berson and M. Jones, Jr., *J. Amer. Chem. Soc.*, **86**, 5017, 5019 (1964).

Results

Preparation of *cis*- and *trans*-1-Trimethylsiloxy-1-vinylcyclodec-3-ene (10c and 10t). Cyclooctene was stereospecifically converted to *cis*- or *trans*-cyclodec-3-en-1-ol as described previously[5] except that a modified Simmons–Smith procedure[6] was used. Oxidation gave the ketone which was treated with vinylmagnesium bromide to give the desired alcohol cleanly in good yield. The siloxy derivative was prepared as before.[3]

Thermolysis of 10c and 10t. When either **10c** or **10t** is heated in evacuated sealed ampoules at 240–305° a mixture of at least six isomeric rearrangement products results which is only partially separable by capillary gc. These appear to be various stereoisomeric trimethylsilyl enol ethers.[3] Hydrolysis of the mixture gives only the *cis*- and *trans*-cyclododec-5-en-1-ones (**12c** and **12t**) and 4-vinylcyclodecanone (**11**). The product structures were assigned from spectral data and by analogy with the nine-membered ring case. There was no observable interconversion of **10c** and **10t** under the reaction conditions. Such interconversion would have been readily seen since the capillary gc peaks for the alcohols corresponding to **10c** and **10t** were well resolved. The ratios of products from **10c** and **10t** were not the same (see Scheme I). In each case, the

Scheme I. Products Formed from **10c** and **10t** upon Thermolysis at 300–310° Followed by Hydrolysis



stereochemistry of the ring double bond is largely retained in the ring expanded product but some geo-

(5) C. D. Poulter and S. Winstein, *ibid.*, **92**, 4282 (1970).

(6) R. W. Thies, M. Gasic, D. Whalen, J. B. Grutzner, M. Sakai, B. Johnson, and S. Winstein, *ibid.*, **94**, 2262 (1972).

metric isomerization takes place for both systems. The ratio of products for each system did not change appreciably with temperature over the range examined (243–303°). When heated for longer times, the trimethylsilyl enol ethers corresponding to **12c** and **12t** were shown to interconvert but that process is about tenfold slower than the products are formed (see Table I).

Table I. Interconversion of Products from **10c** and **10t** at 310°

Substrate	Time, hr	Relative percentages of products after hydrolysis **10**	**11**	**12t**	**12c**
10t	0.17	14	10	86	5
	0.5	1	11	83	6
	1.0		11	82	7
	3.0		5[a]	78	17
	24		6[a]	74	21
10c	0.18	44	12	10	78
	2.2		5[a]	15	81
	22.5		1[a]	42	58
	30			50	50

[a] An additional product was formed with long retention time on gc.

Kinetic measurements gave good first-order plots for conversion of **10c** or **10t** to products. Table II presents

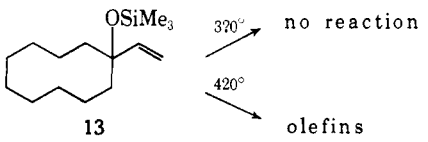
Table II. First-Order Rate of Disappearance of *trans*- and *cis*-1-Trimethylsiloxy-1-vinylcyclodec-3-enes (**10t** and **10c**)

Compd	Temp, °C[a]	10^5k, sec^{-1} [b,c]	Corr coeff
10t	243.5	1.72 ± 0.03	0.997
	243.8	1.81 ± 0.02	0.997
	257.0	3.85 ± 0.01	0.997
	280.0	32.1 ± 0.3	0.997
	E_a = 45.1 kcal/mol		0.993
	$A = 10^{14.28}$		
10c	262.4	1.17 ± 0.01	0.996
	275.5	3.56 ± 0.02	0.994
	295.2	18.6 ± 0.1	0.998
	303.3	34.2 ± 0.1	0.997
	E_a = 50.4 kcal/mol		0.9998
	$A = 10^{15.64}$		

[a] Determined by ASTM thermometer in the $NaNO_2$–KNO_3 fused salt bath or in an aluminum block oven. [b] The rate constant is that obtained by a least-squares plot of 5–15 data points for each temperature. The error is the average deviation of those points from the corresponding line. [c] The material balance was ≥80% as measured by internal gc standard experiments.

the variation of rate with temperature and the resultant activation parameters.

Thermolysis of Systems Related to 10c and 10t. When the ring double bond is removed, the reaction no longer takes place. Thus, thermolysis of 1-trimethylsiloxy-1-vinylcyclodecane (**13**) does not give the

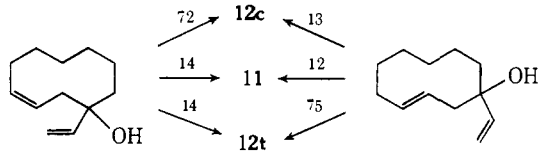


13

siloxy-Cope rearrangement. Under vigorous conditions it forms olefins. Thermolysis of the alcohol related to **13** also gives only olefins.

The alcohols corresponding to **10c** and **10t** give the same behavior as the nine-membered ring analogs. The oxy-Cope products (**11**, **12c**, and **12t**) are formed but the yield is low (*ca.* 20%) and the rates are erratic (Scheme II). Variable amounts of dodeca-1,11-dien-3-one (β-hydroxyolefin cleavage) and olefins are formed as well as polymeric material.

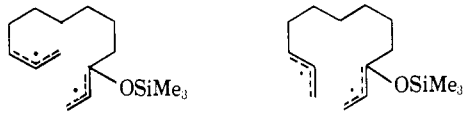
Scheme II. Relative Amounts of Oxy-Cope Rearrangement Products from the Alcohols Corresponding to **10c** and **10t**



Discussion

Attention has recently been focused on whether a diradical is a reasonable intermediate in [1,3] shift rearrangements.[7] It has been argued that three pathways are possible: allowed concerted (*e.g.*, $_\pi2_s + {}_\sigma2_a$),[8] forbidden concerted (*e.g.*, $_\pi2_s + {}_\sigma2_s$), and diradical. Simple molecular orbital calculations were cited which designate diradical formation as the least favorable pathway. Elegant stereochemical labeling studies have indicated that for the bicyclic and small ring systems studied, the diradical plays little if any role.[7,9]

In the present case, diradicals from **10c** and **10t** could be represented as **14** and **15**. Such intermediates



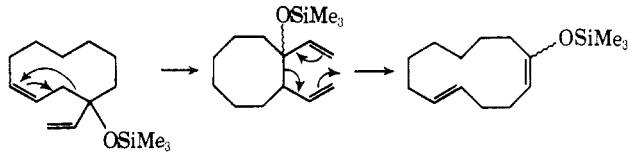
14 **15**

would be consistent with the activation parameters observed; however, the activation parameters for concerted [1,3] shifts have been shown to be essentially the same as the predicted values for a diradical.[7] The diradicals could also explain the formation of geometrically isomerized products (*e.g.* **10c** → **12t**). This would require that **14** and **15** partially interconvert before reclosing. Clearly they could not fully equilibrate since the product mixture for **10c** is quite different from that for **10t**. *Thus a single diradical in which the barriers to rotation and allylic radical isomerization are small relative to the barrier to reclosure is ruled out by the present results.*

While **14** and **15** can explain the isomerized products if their interconversion is about tenfold slower than reclosure,[10] the isomerization could also arise by a sequence of concerted reactions (*e.g.*, **10c** → **16** → **12t**). Compound **16** was not observed, but that is expected since it lies higher on the energy surface than **12c** or **12t** and [3,3] shifts are normally faster than [1,3] shifts. This type of process is observable for the eight-membered analog **8**.

The failure of **13** to undergo siloxy-Cope rearrangement could be taken as support for a diradical mech-

(7) J. A. Berson, *Accounts Chem. Res.* **5**, 406 (1972); see also R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **94**, 9107 (1972).
(8) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(9) (a) J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 267, 269 (1973); (b) J. A. Berson and R. W. Holder, *ibid.*, **95**, 2037 (1973).
(10) See discussion in ref 3.



10c 16 12t

anism. The ring double bond in **10c** or **10t** would provide substantial stabilization for **14** and **15** which would be lacking in a diradical derived from **13**. Again this could be consistent with a concerted reaction. Berson and Holder[7,9b] have examined a system in which the stereochemical control indicates a concerted [1,3] shift but where a carbonyl next to the migrating center lowers the activation energy by 9 kcal/mol.

A comparison of the activation parameters for the rings that we have studied suggests a concerted mechanism. Thus Table III compares the activation energies

Table III. Energy Comparisons for Medium-Sized Ring Siloxy-Cope Rearrangements

Compd	Ring[a] strain, kcal/mol	E_a, kcal/mol	Overall ΔH,[d] kcal/mol
8	6.7	53.9[b]	~−3[e]
10c	7.4	50.4	~−12
9	10.5	47.7[c]	~−10
10t	10.7	45.1	~−15

[a] The ring strains are those for the simple cycloalkenes: S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; J. Sicher, *Progr. Stereochem.*, **3**, 202 (1962); R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957)]. [b] See ref 2. [c] See ref 3. [d] The bond energy changes [estimated by the method of J. D. Cox, *Tetrahedron*, **19**, 1175 (1963)], relief of "skew butane" interactions [S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968], and formation of an enol [S. J. Rhoads and E. E. Waali, *J. Org. Chem.*, **35**, 3358 (1970)] were estimated to favor the [1,3] siloxy-Cope reaction by 8 kcal/mol. The differences from that value result from estimates of the ring-strain charges which are necessarily crude since no thermochemical data are available for the cycloalkadienes. [e] This number corresponds to either [1,3) shift ring expansion or [1,3] shift ring contraction. In fact, both are observed.

with estimated strain energies and overall energy changes. As expected, increased ring strain in the substrate leads to lower activation parameters (compare **8** and **10c** with **9** and **10t**). This would fit a diradical scheme since most of the ring strain could be lost in going to the transition state leading to the open chain diradical. However, a diradical scheme would not explain the 3.5 kcal/mol lower activation energy for **10c** relative to **8**. It appears that the overall energetics of the reaction are also important as would be expected for a concerted process. The same argument could be made for **9** relative to **10t**, although the effect is smaller and the systems more different. These data can only be regarded as suggestive since the error limits for such activation energy measurements have been estimated[11] to be ±1.7 kcal/mol. The comparisons may be better than that since the error limits include systematic errors which should cancel to some extent; however, the ring strain and overall enthalpy changes are only crude estimates since appropriate thermochemical data are not available. Clearly a stereochemical study would be desirable to provide more substantial evidence regarding the mechanism.

Synthetic Considerations. If there is a diradical in these rearrangements, it is synthetically unimportant inasmuch as it is not trappable when the reactions are run neat or in toluene.[2,3] The influence of ring strain is of importance since it affects the rate of reaction which in turn governs the temperatures that must be used. This could be a deciding factor since it is clear from the study of **13** that at higher temperatures, other reactions can compete. The overall energetics also appear to affect the rate. From the available thermochemical data, the expansion of a seven-membered ring appears to be borderline while the large rings seem feasible, although the activation barriers for the large rings could be high enough to cause problems with competing side reactions. A large ring system is currently under investigation.

Experimental Section

General. Spectra measurements utilized Beckman IR8, Varian Associates HA100, Atlas CH7, and CEC 110B[12] instruments. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium.

Gas Chromatography. Sample purification utilized an Aerograph Model A-90-P with the following 0.25-in. columns: (A) 12 ft, 5% Carbowax 4000 on 110–120 Anachrome; (B) 6 ft, 5% Carbowax 4000 on 60–80 Chromosorb W; and (C) 17 ft, 10% SF96 on 70–80 Chromosorb G. Analytical gc was carried out with a Varian-Aerograph Model 1200 with much more efficient 0.01-in. capillary columns: (D) 75 ft, DEGS; (E) 125 ft, UCON LB 550X; (F) 100 ft, Apiezon N. Peak areas were measured with a Hewlett-Packard Model 3373 B integrator.

***cis*- and *trans*-cyclodec-3-en-1-ol** were prepared as described by Poulter and Winstein[5] except that LeGoff couple[13] was used for the Simmons–Smith step which gave comparable results except that the reaction was slower.[14]

***trans*-1-Vinylcyclodec-3-en-1-ol.** ***trans*-Cyclodec-3-en-1-ol** was oxidized in 76% yield by the previously described procedure[3] to the corresponding ketone: ir (neat) 2945, 2070, 1695, 1450, 1435, 1340, 1250, 1163, 1100, and 980 cm^{-1}. The ketone was then reacted with vinylmagnesium bromide as detailed earlier.[3,15] The product was purified by column chromatography on SilicAR using 2–10% ether–pentane eluent which gave a 66% yield of the desired vinyl alcohol: ir (neat) 3420, 3020, 2940, 2870, 1470, 1445, 1055, and 985 cm^{-1}; nmr (δ, CCl_4) 5.87, 5.09, 4.86 (ABC pattern, J = 1.5, 10, and 17.5 Hz, 3), 5.3–5.5 (m, 2), 1.1–2.3 (m, 15).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.85; H, 11.04.

***trans*-1-Trimethylsiloxy-1-vinylcyclodec-3-ene (10t).** In a typical preparation, 0.6 g of *trans*-1-vinylcyclodec-3-en-1-ol was mixed with 1.8 ml of dry DMSO and 1.2 ml of Tri-Sil Concentrate (Pierce Chemical Co). The mixture was shaken for 10 min and the upper layer separated. The lower layer was washed with one 2-ml portion of pentane and combined with the upper layer. The combined layers were washed with one 2-ml portion of water. The resulting pentane solution was dried over anhydrous magnesium sulfate. The product was collected by preparative gc using column C at a temperature of 185° and a helium flow of 60 ml/min. The yield of clear liquid was 0.49 g (61%): ir (neat) 3030, 2970, 2890, 1450, 1410, 1245, 1055 (broad), 985, 918, 835, and 752 cm^{-1}; nmr (δ, CCl_4) 5.87, 4.93, 4.84 (ABC pattern, J = 1.5, 10.5, and 17.5 Hz, 3), 5.2–5.4 (m, 2), 1.3–1.9 (m, 14), 0.06 (s, 9).

Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. Found: C, 71.11; H, 10.97.

(11) S. W. Benson and H. E. O'Neil, "Kinetic Data on Gas-Phase Unimolecular Reactions," NSRDS, NBS-21, U. S. Government Printing Office, Washington, D. C., 1970.

(12) We thank the University of Oregon for the use of this instrument.

(13) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(14) For experimental details of conditions for these Simmons–Smith reactions, see ref 6.

(15) Vinyllithium gave similar results but vinylmagnesium chloride gave a serious side reaction: J. E. Billigmeier Ph.D. Dissertation, Oregon State University, 1973.

cis-**Cyclodec-3-en-1-one.** Oxidation[3] of *cis*-cyclodec-3-en-1-ol gave a 62% yield of the desired ketone: ir (neat) 3000, 2930, 2860, 1660, 1475, 1435, 1335, 1285, 1200, 1162, 1035, 848, and 724 cm^{-1}; nmr (δ, CCl_4) 5.3–5.9 (m, 2), 3.0 (d, J = 7 Hz, 2), 2.0–2.6 (m, 4), 1.8–1.2 (m, 8).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.93; H, 10.54.

cis-**1-Vinylcyclodec-3-en-1-ol.** The procedure used was the same as for the trans series and gave a 54% yield of the desired vinyl alcohol: ir (neat) 3480, 3050, 2950, 2845, 1480, 1455, 995, 885, 795, 730, 718, and 700 cm^{-1}; nmr (δ, CCl_4) 5.92, 5.16, 4.95 (ABC pattern, J = 1.5, 10, and 18 Hz, 3), 5.3–5.7 (m, 2), 1.1–1.8 (m, 15).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.76; H, 11.17.

cis-**1-Trimethylsiloxy-1-vinylcyclodec-3-ene (10c).** The method outlined for **10t** was also used to give a 61% yield (after preparative gc) of **10c**: ir (neat) 3120, 3025, 2980, 2860, 1470, 1435, 1410, 1250, 1062, 918, 835, and 750 cm^{-1}; nmr (δ, CCl_4) 5.85, 5.09, 4.99 (ABC pattern, J = 1.5, 10, and 18 Hz, 3), 5.2–5.6 (m, 2), 1.2–3.0 (m, 14), and 0.08 (s, 9).

Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. Found: C, 71.52; H, 11.06.

Thermolyses were run in the gas phase in evacuated Pyrex ampoules as described previously.[3] The products were hydrolyzed[3,16] and separated by gc on columns A and C.

Structural Assignments. The thermolyses of **10c** and its corresponding alcohol give a set of products with gc and spectral data that are analogous to the corresponding data for the products formed from the nine-membered ring case examined earlier. The products from **10t** and its alcohol were the same as for the cis cases except that the ratio of **12c** and **12t** was approximately reversed. The spectra of the products are listed below.

cis-**Cyclodec-5-en-1-one (12c):** ir (neat) 3050, 2980, 2920, 1700, 1460, 1445, 1430, 1365, 1162, 1100, 1010, and 693 cm^{-1}; nmr (δ, CCl_4) 5.1–5.4 (m, 2), 2.2–2.6 (m, 4), 1.0–2.2 (m, 14).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.90; H, 11.03.

trans-**Cyclodec-5-en-1-one (12t):** ir (neat) 3120, 2970, 2920, 1705, 1445, 1365, 1160, 1072, and 982 cm^{-1}; nmr (δ CCl_4) 4.9–5.1 (m, 2), 2.2–2.4 (m, 4), 1.0–2.2 (m, 14).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.74; H, 11.06.

4-Vinylcyclodecanone (11): ir (neat) 3090, 2920, 2860, 1690, 1620, 1460, 1425, 1410, 1360, 1250, and 905 cm^{-1}; nmr (δ, CCl_4) 5.57 (m, 1), 4.91 (d, J = 18 Hz, 1), 4.86 (d, J = 8 Hz, 1), 1.2–2.6 (m, 17); mass spectrum m/e 180.151 (calcd m/e for $C_{12}H_{20}O$, 180.151).

Dodeca-1,11-dien-3-one: nmr (δ, CCl_4) 5.5–6.4 (m, 4), 4.7–5.1 (m, 2), 2.3–2.6 (m, 2), 1.9–2.3 (m, 2), and 1.1–1.8 (m, 10).

Kinetic Experiments. A series of ampoules were heated in either a fused salt bath maintained by a Bailey Model 124 proportional controller or in an aluminum block oven regulated by a Cole Palmer Model 1300 proportional controller. All runs for **10c** used the fused salt bath. The runs for **10t** used both and it was established that both devices gave the same rate at the same measured temperature. Each sample was hydrolyzed[16] and analyzed on columns D and E. The data were treated as before.[3]

Acknowledgment. We thank Research Corporation for Cottrell Research Grant support.

(16) S. Friedman and M. L. Kaufman, *Anal. Chem.*, **38**, 144 (1966).

Substituent Effects on the Generation, Structural Rearrangement, and Deargentation of Argento Carbonium Ions. A Kinetic and Product Study of the Silver(I)-Catalyzed Isomerization of C_1-Functionalized Tricyclo[4.1.0.0^{2,7}]heptanes[1]

Leo A. Paquette and Gerald Zon[2]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received July 26, 1973*

Abstract: The $AgClO_4$-promoted isomerizations of 1-isopropyl-, 1-*tert*-butyl-, several 1-methoxymethyl-, and 1-(2-methoxyethyl)tricyclo[4.1.0.0^{2,7}]heptanes have been examined in detail. Evidence is presented that 1,2-hydride and alkyl shift to argento carbonium ion centers from suitably constructed side chains competes favorably with migration of the allylic cyclohexene hydrogen. The distributions of products from these derivatives have been compared to those of the parent hydrocarbon and several methyl congeners. An increase in effective steric bulk of the 1 substituent leads to an increase in type γ rearrangement (leading to bicyclo[3.2.0]hept-6-enes) at the expense of type α bond reorganization (1,3-cycloheptadiene production). Deuterium isotope effect studies for 1-methoxymethyl-d_3-tricyclo[4.1.0.0^{2,7}] heptane have demonstrated that, although the β' rearrangement is overwhelmingly favored in this instance, fractionation factors very similar to those previously found for the 1-trideuteriomethyl example were measured, signifying that the rate-determining steps in both cases were comparable. Kinetic data also support these conclusions. An overall mechanistic picture is presented which provides a reasonable explanation of the fact that cis enol ethers dominate over their trans counterparts when the type β' mechanism is operative.

The ability of the bicyclo[1.1.0]butane ring system to undergo transition metal catalyzed isomerizations is well documented.[3] The multiplicity of reaction manifolds available to such molecules is exemplified by the behavior of tricyclo[4.1.0.0^{2,7}]heptane deriva-

(1) Part XX of the series dealing with Ag^+-catalyzed rearrangements. For the previous paper, see L. A. Paquette and M. J. Kukla, *J. Chem. Soc., Chem. Commun.*, 409 (1973).

(2) National Institutes of Health Postdoctoral Fellow, 1972–1973.

(3) Reviews of this subject are available: L. A. Paquette, *Accounts Chem. Res.*, 4, 280 (1971); *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci. Org. Chem., Ser. One*, in press.