Siloxy-Cope and Oxy-Cope Rearrangements of the *cis*-1-Vinylcyclooct-3-en-1-ol System

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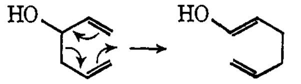
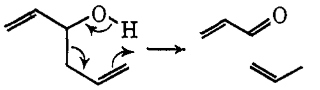
Abstract: *cis*-1-Vinylcyclooct-3-en-1-ol (**1**) ring expands thermally to give *cis*- and *trans*-5-cyclodecenones which rearrange to *cis*- and *trans*-bicyclo[5.3.0]decan-2-ones. β-Hydroxyolefin cleavage and elimination also take place. In contrast, the siloxy derivative, **1**-TMS, undergoes predominant ring contraction to *cis*- and *trans*-1-trimethylsiloxy-1,2-divinylcyclohexanes which rearrange to ring-expanded products. The siloxy variation gives high yields. The activation parameters are consistent with a diradical intermediate but a sequence of concerted reactions can also fit the data.

Open-chain 3-hydroxy-1,5-hexadiene systems undergo only two thermal rearrangements: a [3,3] sigmatropic shift leading to an enol (eq 1) and β-hydroxyolefin cleavage (eq 2).[1] In contrast, certain ring systems have been shown to undergo a third rearrangement, a [1,3] sigmatropic shift leading to an enol (eq 3).[2–5] Both sigmatropic shifts leading to enol forms (eq 1 and 3) have been termed oxy-Cope rearrangements.[5] The enol formation is an important driving force for the reaction (*ca.* 4.5 kcal/mol).[6] A fourth rearrangement, a [1,3] sigmatropic shift that does not lead to an enol (eq 4), was suggested in an earlier investigation of a nine-membered ring system although such a product was not isolable for that system.[4] We now report a study of the eight-membered system which is more complex than the nine-membered one. One interesting aspect is that the pathway shown in eq 4 represents an important pathway, at least for the siloxy derivative.



(1)



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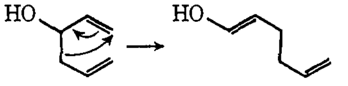

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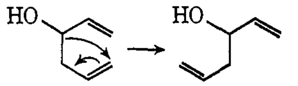


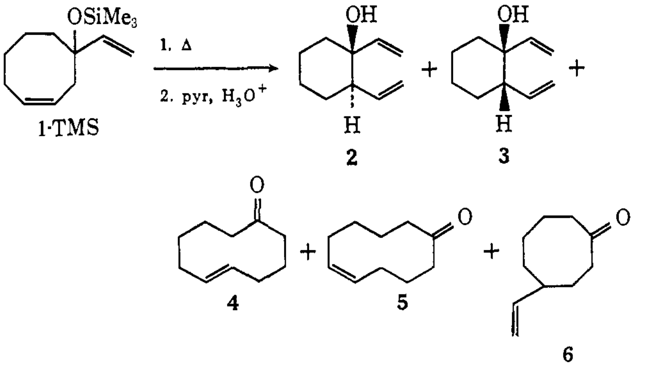
(4)

Results

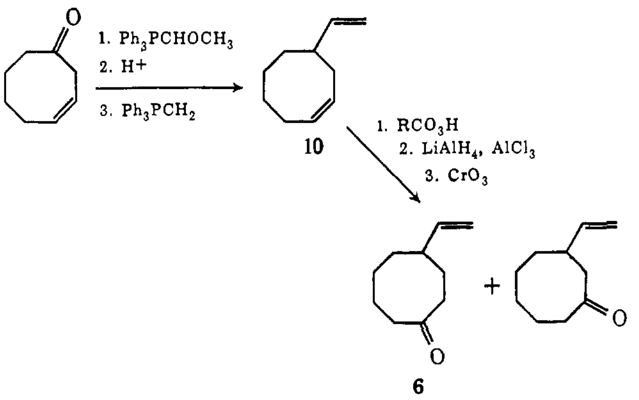
cis-Cyclooct-3-en-1-ol was prepared by hydride reduction of the monoepoxide of 1,3-cyclooctadiene.[7,8] Oxidation followed by treatment with vinylmagnesium bromide gave the desired substrate, *cis*-1-vinylcyclooct-3-en-1-ol (**1**). Treatment with Tri-Sil (Pierce Chemical Co.) in dimethyl sulfoxide gave the trimethylsilyl derivative **1**-TMS.

Thermolysis of **1**-TMS generates a complex mixture of rearranged trimethylsilyl compounds. Hydrolysis of the mixture leads to five components (**2**–**6** in Scheme I). The structures of **2**–**5** were assigned by spectral comparison with authentic samples.[9–11] The structure of **6** was confirmed by synthesis using the route shown in Scheme II.

Scheme I



Scheme II



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[1] A. Viola, E. J. Iorio, K. Chen, G. M. Glover, U. Nayak, and P. J. Kiocienski, *J. Amer. Chem. Soc.*, **89**, 3462 (1967).

[2] R. W. Thies and M. T. Wills, *Tetrahedron Lett.*, 513 (1970).

[3] R. W. Thies, *Chem. Commun.*, 237 (1971).

[4] R. W. Thies, *J. Amer. Chem. Soc.*, **94**, 7074 (1972).

[5] J. A. Berson and M. Jones, Jr., *ibid.*, **86**, 5017, 5019 (1964).

[6] S. J. Rhodes and E. E. Waali, *J. Org. Chem.*, **35**, 3358 (1970).

[7] A. C. Cope and P. E. Peterson, *J. Amer. Chem. Soc.*, **81**, 1643 (1959).

[8] N. Heap and G. H. Whitman, *J. Chem. Soc. B*, 164 (1966).

[9] We thank E. N. Marvell and W. G. Whally for authentic samples of **4**, **5**, **7**, and **8**. The properties have been reported previously.[10,11,23]

[10] H. L. Goering, W. D. Clossen, and A. C. Olson, *J. Amer. Chem. Soc.*, **83**, 3507 (1961).

[11] A. C. Cope and G. Holyman, *ibid.*, **72**, 3062 (1950); A. C. Cope, M. Brown, and H. H. Lee, *ibid.*, 77, 2855 (1955).

Table I. Relative Per Cent of Products Formed from Thermolysis of **1**-TMS Followed by Hydrolysis[a]

Temp, °C	Time, hr	**1**	**2**	**3**	**4**	**5**	**6**	Other
280.5	1	96	1.7	2.0	0.14	0.26	0.09	
281.8	16	78	9.1	6.4	1.1	1.5	2.4	1
281.8	28	67	14.8	10.3	1.6	2.6	3.3	
281.8	33.5	59	15.3	10.9	2.4	7.1	5.0	
281.8	51	39	20.9	14.5	3.6	11.3	7.3	2
316.1	0.5	84	5.1	5.4	1.0	2.0	2.3	
316.1	1.5	63	14.4	10.7	2.6	3.2	4.3	2
316.1	2	55	17.6	12.8	3.2	4.3	5.7	3
316.1	4	28	28.3	19.8	4.4	6.7	9.0	4
337.2	0.5	44	21.6	15.7	3.3	6.4	6.4	2
337.2	0.67	35	25.0	18.2	3.6	7.4	8.9	3
337.2	1.0	22	31.9	23.0	4.5	5.7	10.5	2
337.2	0.5[b]	48	15.1	10.5	3.2	17.5	5.6	

[a] The data shown are representative individual points. The values for **2** and **3** are corrected for losses that occur during hydrolysis. The correction was made by measuring the percentages of **2**-TMS and **3**-TMS before hydrolysis. [b] This sample is typical of those not purified by glc. Samples with a higher sample size to ampoule size ratio and samples run in toluene sometimes gave similar behavior.

The rate at which **1**-TMS converts to products **2**-TMS–**6**-TMS in the gas phase was measured by the ampoule method, analyzing the samples by gas chromatography (Table I). The conversion of **1**-TMS could be examined before hydrolysis since **1**-TMS was separable from the other components. The products **2**-TMS and **3**-TMS were also well separated, whereas the others overlapped badly with each other. The material balance before hydrolysis was nearly quantitative. In earlier work,[4] the rates for the nine-membered case were measured after hydrolysis. This was also tried for **1**-TMS but the rates measured in that way are less certain because **2** and **3** are somewhat unstable to the hydrolysis conditions (**2** is especially labile). The material balance was only about 70%. When corrections were made for losses of **2** and **3** the rates measured in this way were within 6% of the rates measured with unhydrolyzed samples, and the activation parameters calculated from those rates were essentially the same as from those measured before hydrolysis.

Table II shows the rates and activation parameters for the disappearance of **1**-TMS. Linear first-order plots were obtained and the rates were insensitive to ampoule preparation, sample size, and whether or not the samples were purified by preparative gas chromatography. The ampoules must be dry to prevent hydrolysis of the trimethylsilyl group.

Table II. First-Order Rate of Disappearance of 1-Trimethylsiloxy-1-vinylcyclooct-3-ene (**1**-TMS)

Temp,[a] °C	10^5k,[b] sec^{-1}	Correlation coefficient
327.2	38 ± 7	0.9912
316.1	8.1 ± 0.4	0.9986
281.8	0.45 ± 0.04	0.9863
	E_a = 53.89	0.9999
	Log A = 15.88	

[a] Determined by ASTM thermometer in a $NaNO_2$–KNO_3 fused salt bath. [b] The rate constant is that obtained by least-squares fit of 11–14 data points for each temperature. The error is the average deviation from the corresponding line. [c] Internal glc standard experiments indicated a nearly quantitative material balance for the thermolysis. Duplicate independent rate measurements differed by less than 5%.

The interconversion of products was studied, but surprisingly the interconversion was not as well behaved as the rate of disappearance of **1**-TMS. For example, samples that were not purified by glc gave the same conversion of **1**-TMS to products as a purified sample but gave appreciably more ring-expanded products (**5**-TMS was especially enhanced relative to **2**-TMS and **3**-TMS). The same behavior was sometimes seen with larger sample size to ampoule size ratios, and when pyrolyses were carried out in toluene solvent (Table I, last entry) the general trends for purified samples in the same concentration as that used for the kinetic studies are shown in Table III. Nearly the same equilibrium mixture of products can be reached starting with **1**-TMS, a mixture of **2**-TMS and **3**-TMS, or a mixture of **4**-TMS, **5**-TMS, and **6**-TMS. The equilibrium is complex, with some steps being considerably faster than others. In particular, the interconversion of **2**-TMS and **3**-TMS takes place about 40 times faster than they are formed. The overall product equilibrium is approached at a rate comparable to that for product formation.

Table III. Interconversion of the Products of Rearrangement of **1**-TMS

Compound	Temp, °C	Time, hr	*trans*-**2**-TMS	*cis*-**3**-TMS	**4**-TMS–**6**-TMS[a]
2-TMS	285	1	78	18	4
	285	2	71	25	4
	285	3	62	29	9
	285	5	60	31	9
	285	6	54	32	14
	285	7	55	35	9
64% **2**-TMS 35% **3**-TMS	280.5	1	70	18	11[b]
68% **2**-TMS 32% **3**-TMS	281.8	3	54	34	12
		7	48	32	20
		12.5	41	27	32
		120	22	13	65[c]
Mix of **2**-TMS– **4**-TMS **1**-TMS	350	1.25	12	9	68
	340	5	18	10	72[d]

[a] The last entry also contains **1**-TMS. [b] The ratio of **1**:**4**:**5**:**6** after hydrolysis was 0:51:49:0. [c] The ratio of **1**:**4**:**5**:**6** after hydrolysis was 0:11:67:22. [d] The ratio of **1**:**4**:**5**:**6** after hydrolysis was 7:6:63:24.

Because the origin of the trans ten-membered compound **4**-TMS was of particular interet, a further prod-

Table IV. Relative[a] Per Cent of Five Ketone Products[b] Formed from Thermolysis of **1**-OH at 340°

Time, hr	Conversion	**4**	**5**	**6**	**7**	**8**
0.5	34	31	44	4	18	3
1	89	19	38	4	30	9
2	100	9	34	7	26	25
3	98	6	33	4	32	25
4	100	7	33	7	26	27

[a] Total yield *ca.* 16%. [b] Olefins, cleavage product **9**, and at least six minor products are also formed.

uct interconversion study was carried out in which separate samples of **1**-TMS and the divinyl products (**2**-TMS and **3**-TMS) were heated for 1 hr at 280.5°. This gives 4% conversion of **1**-TMS to a product mixture in which 3.7% is **2**-TMS and **3**-TMS and 0.14% is the trans ten-membered compound **4**-TMS. Under the same conditions, the sample of **2**-TMS and **3**-TMS gave 5.7% conversion to **4**-TMS. This means that the **2**-TMS and **3**-TMS formed from **1**-TMS could produce a maximum of 0.23% of **4**-TMS during this time period; *i. e.*, all the **4**-TMS could arise from **2**-TMS and **3**-TMS.

Thermolysis of the alcohol **1** gives a complex product mixture from which six isomeric ketones were isolated and identified (Scheme III). Products **4**–**8** were identified by spectral comparison with authentic samples.[9-11] Deca-1,9-dien-3-one (**9**) was identified by the infrared (C=O, 6.0 μ) and nmr spectra (two overlapping terminal vinyl patterns). The assignment is supported by the mass spectrum, which shows prominent peaks for fragments corresponding to cleavage α to the carbonyl group and for McLafferty rearrangement.

Scheme III

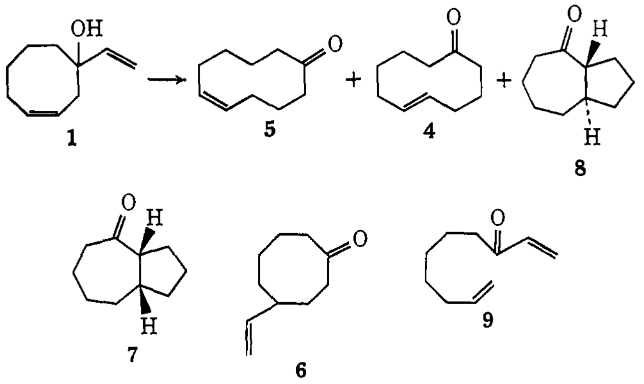


Table IV shows the variation with time in the relative amounts of five products that are formed in approximately 16% yield. Since the products do not polymerize appreciably, the composition would stay constant if no product interconversions were taking place. The changes observed indicate that the cyclodecenones **4** and **5** or their enol precursors rearrange to the bicyclo[5.3.0]decan-2-ones, **7** and **8**. At long reaction times (20 hr, 340°) the latter comprise 85% of the volatile products, while most of the remaining 15% appears to be a mixture of *cis*- and *trans*-bicyclo[4.4.0]decan-2-ones.

The ketone products were shown to interconvert under the reaction conditions. Heating a sample of **5** at 350–360° for 2.5 hr gave 70% conversion to **7** and **8**. Heating **8** under similar conditions caused 20% isomerization to **7**.

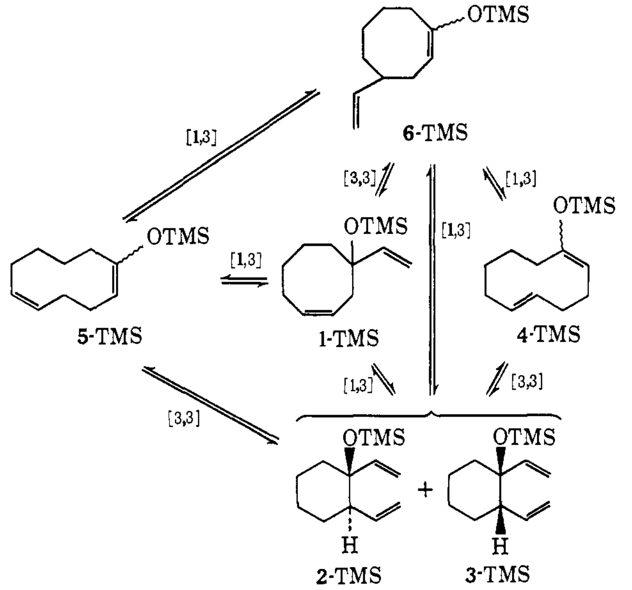
Products other than those shown in Table IV are also formed. After 1 hr at 350°, glc analysis shows approximately 37% of products **4**–**8**, 16% of cleavage product **9**, 12% of at least six other unknown components with retention times similar to **9**, and 35% of olefins. Product **9** is probably formed in much greater amounts than are observed since it polymerizes readily. No 1,2-divinylcyclohexan-1-ols (products that would result from eq 4) were observed, but these compounds are not stable to the reaction conditions.

The rearrangement of *cis*-4-vinylcyclooctene (**10**) was examined briefly. *cis*- and *trans*-1,2-divinylcyclohexanes are the major products, but other unknown products are also formed. No 1,5-cyclodecadienes were observable; however, it has been shown previously that they rearrange rapidly and completely (>99.7%) to the 1,2-divinylcyclohexanes.[12]

Discussion

The rearrangements of **1**-TMS are similar in many respects to those of the nine-membered analog reported earlier.[3,4] The major difference is that **1**-TMS gives observable products, **2**-TMS and **3**-TMS, that result from a [1,3] sigmatropic shift ring contraction (Scheme IV). Unlike the nine-membered case, the ring contraction products are of comparable energy to ring-expanded ones. For **1**-TMS, the principal driving force for formation of **2**-TMS and **3**-TMS is relief of ring strain (*ca.* 6 kcal/mol),[13,14]

Scheme IV[16]



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(12) (a) C. A, Grob, H. Link, and P. W. Schiess, *Helv. Chim. Acta*, **46**, 483 (1963); (b) P. Heimbach, *Angew. Chem.*, **76**, 859 (1964); *Angew. Chem., Int. Ed. Engl.*, **2**, 113 (1963).

(13) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(14) Other smaller effects are also involved, *viz.*, bond energy changes,[15] "skew butane" interactions, and entropy changes. The sum of these effects is favorable for ring expansion (*ca.* 4 kcal/mol) and unfavorable for ring contraction (*ca.* 2 kcal/mol). For 1-TMS, ring strain changes are probably unfavorable for ring expansion, but the magnitude is difficult to estimate since thermochemical data for 1,5-cyclodecadienes are not available.

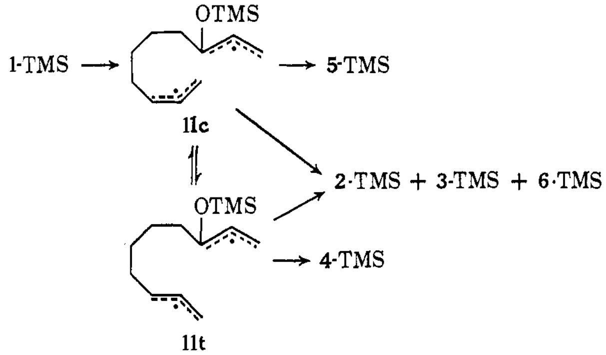
(15) Estimated by the method of J. D. Cox, *Tetrahedron*, **19**, 1175 (1963).

(16) The trimethylsilyl enol ethers are shown with a wavy line to indicate that the enol double bond can be cis or trans or a mixture of both.

whereas the ring-expanded products are favored by enolate formation (*ca.* 4.5 kcal/mol[6]). In the nine-membered ring, the ring strain released in ring contraction is much less, which accounts for the lack of observable divinylcycloheptane products. The importance of enolate formation is shown by the thermolysis of *cis*-4-vinylcyclooctene (**10**) that gives ring contraction but not ring expansion; *i.e.*, it is dominated by the ring strain changes.[12]

Sigmatropic shifts interrelating **1**-TMS and its isomeric products are shown in Scheme IV. In this scheme all products could be formed from **1**-TMS by a one-step concerted rearrangement except for **4**-TMS. The trans double bond in **4**-TMS requires that it be formed in a sequence of sigmatropic shifts or from a diradical **11** in which geometric isomerization competes with reclosure[17] (Scheme V).

Scheme V

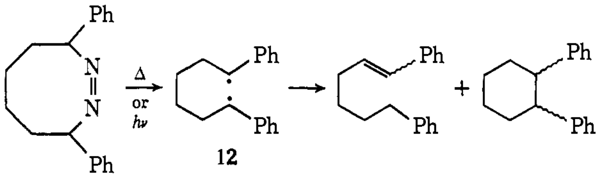


The viability of a sequential mechanism depends on the relative rates of product interconversion. The most likely sequence involves **2**-TMS and **3**-TMS. Since **4**-TMS is formed even at very low conversion, the [3,3] shift step from **2**-TMS and **3**-TMS would have to be fast relative to formation of **2**-TMS and **3**-TMS. The data in Table III indicate that this is the case. The *trans*-divinyl compound **2**-TMS interconverts with **3**-TMS about 40 times faster than **1**-TMS rearranges to products. A likely mechanism for the interconversion of **2**-TMS and **3**-TMS would be a [3,3] shift rearrangement leading to the ten-membered ring compounds, followed by a conformational change and then a [3,3] rearrangement back to the other isomer.

The data in Table III indicate that formation of **4**-TMS and **5**-TMS from **2**-TMS is not a simple first-order process. Heating **2**-TMS gives rapid formation of a relatively small amount of **4**-TMS and **5**-TMS, but then slowly an equilibrium is reached which favors the latter compounds. Since the final equilibrium involves **2**-TMS, **3**-TMS, and four stereoisomers of the ten-membered ring compounds, nonlinear behavior is not unexpected. The slow attainment of an equilibrium favoring the ten-membered ring compounds suggests that the transition state leading to the most stable isomer is not as readily accessible. Models suggest that the cis,cis isomer may be more stable and it can only be formed through a boat-like transition state which is known to be much less favorable[18] than the chair. In support of this, the cis compound **5** is the predominant product in the hydrolyzed samples heated for long times.

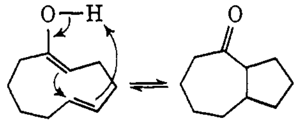
It was established that in the time period corresponding to 4% conversion of **1**-TMS, sufficient **4**-TMS can be formed from **2**-TMS to account for all the **4**-TMS formed from **1**-TMS. In other words, it is not necessary to postulate a diradical capable of geometric isomerization to accommodate the data for this system.

As was the case in the nine-membered system, the activation parameters are consistent with formation of a diradical; however, that criterion does not rule out concerted reactions.[19] Recent work on *trans*-divinylcyclobutane systems[19] suggests that concerted reactions are favored relative to diradical ones, even when they are forbidden by orbital symmetry.[20] The rearrangements for this system could all be concerted although certain steps such as the [1,3] shift converting **1**-TMS to **2**-TMS or **3**-TMS would probably have to go by the symmetry forbidden pathway because of the large groups on the migrating center.[16] We cannot conclusively rule out diradical intermediates for this reaction but if they are formed they behave differently than related diradicals (*e.g.*, **12**) generated from 3,8-diphenyl-1,2-diaza-1-cyclooctene.[21] In that diradical, a major pathway is internal hydrogen abstraction, a process that we do not observe with **1**-TMS. Attempts to trap a diradical formed from **1**-TMS using toluene as a solvent were also negative.[16]



The products from thermal rearrangement of **1** are quite different from **1**-TMS. The [1,3] shift ring contraction products **2** and **3** were not found but this could be misleading since those products are quite unstable to the pyrolysis conditions employed.[22] Two new products, **7** and **8**, are formed by rearrangement of **4** and **5** or their enol forms.[24] A likely mechanism is shown in Scheme VI. The rearrangements of the enol leading to **7** and **8** or to the ketones **4** and **5** are energetically quite favorable (>5 kcal/mol). However, they are reversible under the reaction conditions as evidenced by the interconversion of **5**, **7**, and **8**. A reasonable mechanism for the interconversion of **7** and **8**

Scheme VI



7 or **8**

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[17] See earlier discussion.[4]

[18] M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 7147 (1972).

[19] J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972).

[20] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[21] C. G. Overberger, J. W. Stoddard, C. Yaroslavsky, H. Katz, and J. P. Anselm, *J. Amer. Chem. Soc.*, **91**, 3226 (1969).

[22] In solutions **2** and **3** rearrange smoothly at 220° to cyclodecenones.[23] Under the conditions used here, only about 10% of **2** and **3** is converted to cyclodecenone, with the remainder going to olefins and nonvolatile material.

[23] E. N. Marvell and W. Whalley, *Tetrahedron Lett.*, 509 (1970).

[24] For related rearrangements, see (a) M. Urion, *Ann. Chim.*, **1**, 5 (1934); (b) E. Brown, P. Leriverend, and J. M. Conia, *Tetrahedron Lett.*, 6115 (1966); (c) E. N. Marvell and W. Whalley, *ibid.*, 1337 (1969).

would be rearrangement to the enol, conformational change, and rearrangement back to the other isomer.

The β-hydroxy olefin cleavage product was isolable, although it is quite unstable to the pyrolysis conditions so that the amount formed is probably much greater than that observed. The much higher yields attained with the siloxy-Cope variation are presumably largely due to preventing this process and inhibiting olefin formations.

In summary, the oxy-Cope and siloxy-Cope rearrangements of this system give quite different products, the difference arising largely because the unblocked hydroxyl group allows other reactions to take place. The siloxy variation gives a cleaner, higher yield reaction. The present data do not provide a clear choice between the diradical and concerted mechanisms.

Experimental Section

General. Infrared spectra were measured on a Beckman IR8 infrared spectrometer. Nmr spectra were measured on Varian Associates A-60 or HA-100 instruments. Mass spectra were obtained on an Atlas CH7 mass spectrometer equipped with a gas chromatograph inlet system. Elemental analyses were performed by Alfred Bernhardt Microanalytisches Laboratorium. Boiling points are uncorrected. Analytical gas-liquid chromatography (glc) utilized a Varian Aerograph Model 1200 instrument with flame ionization detector and injectors for either $^1/_8$ or 0.01-in. capillary columns: column A, 100 ft × 0.01 in. Carbowax 1000; column B, 23 ft × $^1/_8$ in. 0.1% Carbowax 1000 on Corning glc 110. A Hewlett-Packard 3373 B integrator was used to determine peak areas for the kinetic runs. Preparative glc was done with an Aerograph A-90-P instrument: column C, 17 ft × $^1/_4$ in., 10% SF96 on 70–80 Chromosorb G; column D, 7 ft × $^1/_4$ in., 10% DEGS on 60–80 Chromosorb W; column E, 8 ft × $^1/_4$ in., 5% Carbowax 4000 on 110–120 Anachrom.

***cis*-3-Cyclooctenone** was prepared in three steps from 1,3-cyclooctadiene by the previously described method.[7,8]

***cis*-1-Vinylcyclooct-3-en-1-ol (1)** was prepared by the addition of vinylmagnesium bromide in the same way as reported[4] for the nine-membered analog, except that the ketone was added and stirred for 3 hr at room temperature. The product was purified by column chromatography on SilicAR (Mallinckrodt Chemical Co.), which gave a 72% yield of **1**: ir (neat) 2.95, 3.30, 3.40, 3.50, 6.15, 6.85, 10.10, 10.95, 12.20, 13.10 cm^{-1}; nmr (δ CCl_4) 5.9, 5.2, 4.9 (ABC pattern, J = 2, 10, 18 Hz, 3), 5.4–5.8 (m, 2), 3.1 (s, OH), 1.9–2.4 (m, 4), 1.2–1.8 (m, 6).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.91; H, 10.38.

***cis*-1-Trimethylsiloxy-1-vinylcyclooct-3-ene (1-TMS)** was prepared by the method described previously[4] and purified on column C: ir (neat) 3.30, 3.40, 3.48, 8.00, 9.15, 9.45, 10.90, 11.95, 12.95, 13.30 cm^{-1}; nmr (δ CCl_4) 5.8, 5.0, 4.9 (ABC pattern, J = 1, 10, 18 Hz, 3), 5.2–5.8 (m, 2), 1.9–2.4 (m, 4), 1.2–1.8 (m, 6), 0.0 (m, 9).

Anal. Calcd for $C_{13}H_{24}OSi$: C, 69.57; H, 10.78. Found: C, 69.77; H, 10.59.

***cis*-4-Vinylcyclooctene (10).** A 55-ml portion of 0.73 M phenyllithium was added under nitrogen to an ice-cooled solution of 13.7 g of triphenyl(methoxymethyl)phosphonium chloride in 100 ml of ether. After 15 min of stirring, 3.7 g of *cis*-3-cyclooctenone was added to the red solution, which gave a white precipitate. After 2 days of being stirred, the reaction mixture was poured into water. The organic layer was washed twice with water, with brine, and dried ($MgSO_4$). Concentration and vacuum transfer gave 1.7 g of product (57% yield). The aldehyde was generated by swirling for 5 min with 10 ml of 70% perchloric acid and 25 ml of ether, followed by dilution with 200 ml of water.[25] After drying ($MgSO_4$), the crude aldehyde was added to triphenylphosphonium methylide generated from 12 g of triphenylmethylphosphonium iodide, 0.41 ml of 0.73 M phenyllithium, and 75 ml of ether. After 2 days of stirring, work-up as before gave 0.4 g (45% yield) of **10**: nmr (δ CCl_4) 5.3–6.0 (m, 3), 4.90 (d, J = 18 Hz, 1), 4.85 (d, J = 10 Hz, 1), 1.8–2.3 (m, 5), 1.2–1.8 (m, 6).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.07; H, 11.60.

4-Vinylcyclooctanone (6). A solution of 0.115 g (0.76 mmol) of **10** in 5 ml of chloroform was cooled in ice. A solution of 0.17 g of 40% peracetic acid and 76 mg of sodium acetate was added and the reaction was stirred for 2 hr. Sodium sulfite was added until starch–iodine gave a negative test. The organic layer was washed with water and saturated sodium carbonate and then dried over sodium sulfate. The crude epoxide was treated with excess lithium aluminum hydride and 0.5 g of aluminum chloride ($LiAlH_4$ by itself gave no reaction). The reaction was quenched with saturated sodium carbonate. Analysis by glc showed a 60:40 ratio of two vinyl alcohols. Jones oxidation[26] gave two ketones. The major product, separated and purified on columns C and D, was identical with the [3,3] shift product isolated from pyrolysis of **1**: ir (neat) 3.24, 3.40, 3.48, 5.80, 6.15, 10.05, 11.00, 11.80 cm^{-1}; nmr (δ CCl_4), 5.3–6.0 (m, 1), 4.90 (d, J = 17 Hz, 1), 4.85 (d, J = 11 Hz, 1), 2.0–2.6 (m, 5), 1.2–2.0 (m, 8).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.70; H, 10.39.

Thermolyses were run in the gas phase in evacuated ampoules as described in a previous paper.[4] The considerations outlined there were generally true for this system also, but in the present case the siloxy compound was not completely well behaved. The product interconversion was somewhat erratic, generally showing less **2** and **3** and more **5** with samples that were not purified by glc or more concentrated samples or samples run in toluene solution.

The products were analyzed by glc on columns A or B (many other columns tried gave only partial separation). The major products were isolated by repeated fractionation on columns C, D, and E. This gave reasonably pure (>85%) samples of **2**, **3**, **5**, **6**, **7**, and **8** which were shown to match with authentic samples. The glc retention time (column A) and infrared, nmr, and mass spectra were compared for each of these compounds. Melting points of 2,4-DNP derivatives were compared for **5** and **8**. The minor components, **4** and the bicyclo[4.4.0]decan-2-ones, were assigned by glc and mass spectral comparison only. Compound **9** was assigned from its spectral data: ir (neat) 3.23, 3.40, 3.48, 5.90, 5.98, 6.10, 6.20, 7.13, 10.10, 10.40, 11.00 cm^{-1}; nmr (δ CS_2), 6.1–6.3 (m, 2), 5.4–6.0 (m, 2), 4.8–5.1 (m, 2), 2.3–2.6 (m, 2), 1.8–2.3 (m, 2), 1.1–1.8 (m, 6); mass spectrum (70 eV) 152 (parent), 70 (51% of base, McLafferty rearrangement), 55 (base, α cleavage).

Toluene Pyrolyses. Ampoules (10 ml) were charged with 10 mg of **1-TMS** and 1.6 ml of toluene and heated at 281° for 3 hr. No products corresponding to trapped biradical were detected.

Kinetic experiments were performed as described earlier,[4] except that disappearance of **1-TMS** was measured directly rather than as the alcohol. Least-squares plots utilized the equation $\ln (A - A_\infty) = kt + c$, where A_t and A_∞ are per cents of **1-TMS** at time t and time infinity (10 half-lives).

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