Siloxy-Cope[1] and Oxy-Cope[2] Rearrangements of the *cis*-1-Vinylcyclonon-3-en-1-ol System. An Effective Two-Carbon Ring Expansion

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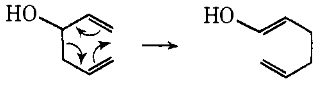
Abstract: Thermal rearrangement of *cis*-1-vinylcyclonon-3-en-1-ol (1-OH) or of the corresponding trimethylsiloxy compound, 1-OTMS, followed by hydrolysis yields mainly *cis*-5-cycloundecenone (5) which represents a [1,3] sigmatropic shift resulting in a two-carbon ring expansion. The minor products result from loss of the cis stereochemistry, a [3,3] sigmatropic shift, and, for the alcohol, β-hydroxy olefin cleavage and elimination. The loss of stereochemistry, rates of reaction, and activation parameters are most consistent with a biradical intermediate. The siloxy variation gives a much higher yield and represents a general way of protecting hydroxyl groups during thermal reactions.

In general, 3-hydroxy-1,5-hexadiene systems can rearrange thermally in four different ways: a [3,3] sigmatropic shift[3] leading to an enol (eq 1), a [1,3] sigmatropic shift leading to an enol (eq 2), a [1,3] sigmatropic shift not leading to an enol (eq 3), and β-hydroxy olefin cleavage (eq 4). All four can be symmetry-allowed rearrangements (*e.g.*, [π^2s + σ^2s + π^2s], [π^2s + σ^2a], [π^2s + σ^2a], and [σ^2s + σ^2s + π^2s], respectively);[3a] however, nonconcerted versions of all are known.[4,5] Both transformations which lead to enol forms (eq 1 and 2) have been termed oxy-Cope rearrangements.[4] Enol formation provides an important driving force for these reactions.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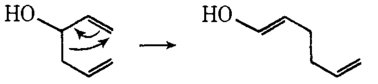
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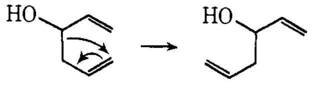
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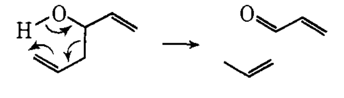
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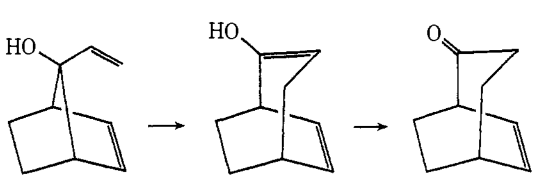
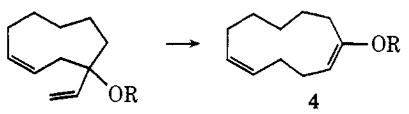
Open-chain systems have been reported[6] to give only the [3,3] shift and cleavage reactions (eq 1 and 4). The lack of [1,3] shift products and the relative ease of the thermal rearrangements have been cited as evidence for concerted reactions. Contrariwise, certain bicyclic systems[4,7] undergo [1,3] oxy-Cope rearrangement as well as the [3,3] oxy-Cope and cleavage reactions (eq 1, 2, and 4). For example, 2 gives predominantly the [1,3] shift product 3. The authors postulate a diradical intermediate.


2
3

The [1,3] sigmatropic shift leading to an enol represents a potentially useful two-carbon ring expansion (*e.g.*, 1-OR → 4). The present study shows that the process is feasible for systems like 1-OR and that the siloxy-Cope variation (R = $Si(CH_3)_3$) gives dramatically improved yields. Kinetic studies on the siloxy-Cope reaction also provide mechanistic information.


1-OR
4

R = H, CH_3, $Si(CH_2)_2$

Results

Preparation of *cis*-1-Vinylcyclonon-3-en-1-ol and the Trimethylsilyl Derivative (1-OH and 1-OTMS). Compound 1-OH was prepared from *cis*-cyclonon-3-en-1-ol[8] by chromic acid oxidation followed by reaction with vinylmagnesium bromide. The trimethylsilyl derivative was prepared by reaction with Tri-Sil[9] in dimethyl sulfoxide.

Thermal Rearrangement of 1-OH. When 1-OH was heated in evacuated, sealed ampoules at about 300° four isomeric compounds were formed along with at least four alkenes. The isomeric compounds were subsequently identified as *cis*- and *trans*-5-cycloundecenone (5 and 6), 4-vinylcyclononanone, (7), and undeca-1,10-dien-3-one (8). The ring structures of 5 and 6 were confirmed by reduction to the known cy-

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[1] Preliminary report: R. W. Thies, *Chem. Commun.*, 237 (1971).

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

[3] Throughout this article, the term "sigmatropic shift" is used to identify an overall bonding change which could take place by either a concerted or a biradical mechanism. This concept has been reviewed: (a) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969); (b) J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968).

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

[5] H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 147 (1966).

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

[7] J. A. Berson and E. J. Walsh, *ibid.*, 90, 4729, 4730, 4732 (1968).

[8] C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, 92, 4274 (1970).

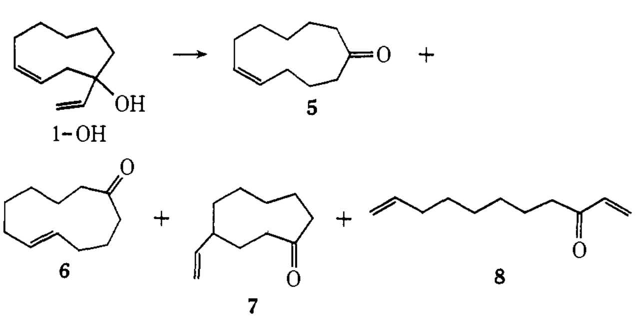
[9] Pierce Chemical Co.

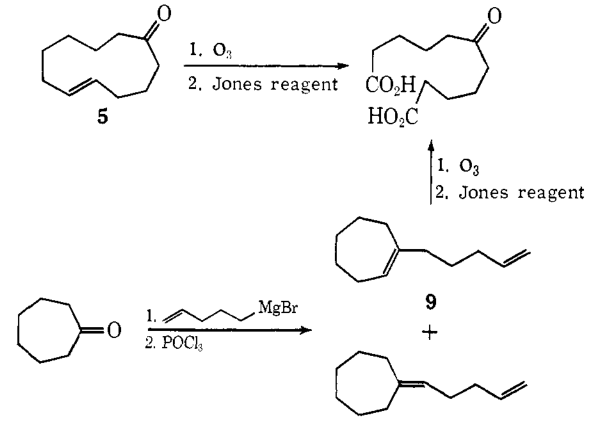
Table I. Products of Thermal Rearrangement[a] of *cis*-1-Vinylcyclonon-3-en-1-ol (1-OH)

Time, hr	Approx conversion, %[b]	Rel amounts of isomeric products[c,d]			
		5	**6**	**7**	**8**
0.25	5–15	55	10	8	26 ± 3
		(74 ± 2)	(15 ± 2)	(11 ± 2)	
0.5	(Not measured)	58	9	8	25 ± 10
		(77 ± 2)	(12 ± 2)	(11 ± 1)	
1.0	25–70	58	11	9	22 ± 3
		(75 ± 1)	(14 ± 1)	(11 ± 1)	
2.0	75–90	66	12	8	14 ± 4
		(77 ± 1)	(14 ± 1)	(9 ± 1)	
4.0	100	76	12	8	4
		(79)	(13)	(9)	

[a] All thermal rearrangements were carried out at 295° with 10 mg of **1-OH** in a 10-ml Pyrex ampoule prepared and sealed as outlined in the Experimental Section. [b] The conversions shown represent the amount of **1-OH** that had been consumed as measured by an internal standard. Two to four samples were run for each time except for the last time where only one was used. [c] Because the amount of **8** is somewhat erratic, the relative amounts of **5**, **6**, and **7** are shown in parentheses. The error shown is the average deviation of two to four independent measurements. Only one measurement was made at 4 hr. [d] Alkenes are also formed in nonreproducable amounts.

cloundecanone. The position of the double bond in **5** was confirmed by ozonolysis which gave the same product as ozonolysis of 1-(4-pentenyl)cycloheptene (**9**).





The stereochemistries of the double bonds in **5** and **6** were assigned from the infrared spectra, *viz.* **5** gave a band at 14.4 μ whereas **6** gave a strong band at 10.25 μ. This criterion has been used previously for medium-sized ring systems.[8,10] As expected,[11] photolysis in benzene interconverts the cis and trans isomers; *i.e.*, **5** isomerizes to a 63:37 mixture of **5** and **6**. The structure of **7** was assigned from the infrared spectrum (C=O, 5.90 μ), the nmr spectrum (the characteristic pattern for the $-CH{=}CH_2$ group), and by analogy with the product from the next lower homolog of **1-OH** where the corresponding product has been independently synthesized.[12] The structure of **8** was assigned from the infrared spectrum (C=O, 5.98) and from the nmr spectrum (two overlapping $-CH{=}CH_2$ patterns). The mass spectral fragmentation pattern supports the assignment. The prominent peaks correspond to the fragments expected for cleavage α and γ to the carbonyl group and for McLafferty rearrangement.

The product ratio was examined as a function of time (Table I). The ratio of **5**:**6**:**7** did not change appreciably with time at a given temperature. Control experiments showed that these three compounds do not polymerize or rearrange appreciably under the reaction conditions. The relative amounts of **1-OH**, **8**, and alkenes were erratic, suggesting that they were affected by nonreproducible surface-catalyzed reactions. In support of this, compound **8** was found to polymerize readily,[13] even at room temperature, and **1-OH** readily eliminates water to form the two major alkenes when subjected to gas chromatography on acidic support.

Ampoules that were prepared by acid washing or sodium hydroxide washing or that were not dried thoroughly gave more elimination than ampoules that were prepared as described in the Experimental Section. Coating the ampoules with silicone oil did not improve the situation. Because of the irreproducible side reactions, it was not possible to obtain reliable rate measurements for the rearrangement of **1-OH**.

The yield of the reaction depends on ampoule preparation and sample size but was never greater than 25%. A definite optimum yield was obtained when the sample size was 10–30 mg/10 ml of ampoule. Samples much larger than this are no longer completely in the gas phase and formation of polymer is readily apparent.

Thermal Rearrangement of 1-OCH$_3$. The thermal rearrangement of the methoxy ether, **1-OCH$_3$**, appeared to give only olefinic products; however, hydrolysis of the pyrolysis mixture revealed that some isomerization to enol ethers does take place. In a run carried out to 91% conversion, approximately 20% of the volatile product was rearranged ether (the ratio of **5**:**6**:**7** after hydrolysis was 69:17:14) and the remainder was ole-

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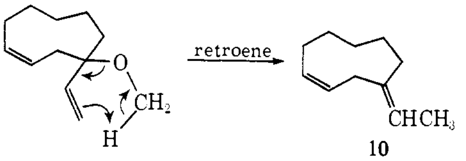
(10) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *J. Amer. Chem. Soc.*, 74, 3643 (1952); A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *ibid.*, 3636 (1952).

(11) M. A. Golub and C. L. Stephens, *J. Phys. Chem.*, **70**, 3576 (1966); M. A. Golub, C. L. Stephens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966).

(12) Unpublished work in these laboratories performed by Dr. M. T. Wills.

(13) This type of compound has previously been shown to be unstable to these reaction conditions: P. Leriverend and J. M. Conia, *Tetrahedron Lett.*, 2681 (1969).

finic. Two isomeric *cis*-4-ethylidenecyclononenes, **10**,



1-OCH$_3$ **10**

which could arise from a retroene rearrangement,[7] comprise 90% of the olefin products. A polymeric coating was observed on the ampoule walls during these pyrolyses.

Thermal Rearrangement of 1-OTMS. Thermal rearrangement of **1**-OTMS gave at least six isomeric products. Isolation of these products proved to be extremely difficult because the reactant and the six isomeric products could only be separated on capillary glc. The products are presumably the six possible trimethylsilyl enol ethers corresponding to [1,3] or [3,3] siloxy-Cope rearrangement. In support of this, the nmr spectrum of the mixture before hydrolysis showed three different trimethylsiloxy peaks near δ 0 and vinyl protons at δ 4.5 (characteristic of enol ethers).[14] Hydrolysis of the mixture gave only the *cis*- and *trans*-cycloundecenones **5** and **6** and the vinylcyclononenone **7** (see Table II). The yield of ring-expanded products **5** and **6** was *ca.* 70% and was not sensitive to sample size. No polymer was observed even when 10% of the ampoule volume was filled with sample (not all in the gas phase).

Table II. Thermal Rearrangement of 1-Trimethylsiloxy-1-vinylcyclonon-3-ene (**1-OTMS**)[a]

T, °C	Time, hr	% conversion	Rel product percentages (after hydrolysis) 5	6	7
296	1.0	47[a]	72	17	12
296	1.0	45	71	16	13
299.0	0.167	21.0	74	12	14
299.0	0.337	35.8	75	12	12
299.0	0.5	49.0	72	15	12
299.0	0.758	63.1	74	16	11
299.0	1.0	74.7	71	18	12
299.0	1.333	80.3	70	21	11
299.0	5.25	100	55	36	10
301.0	11.0	100	43	50	7[b]
301.0	19.5	100	40	54	6[b]
279.5	0.05	1.5	74	10	16
279.5	0.167	5.5	75	12	14
279.5	0.333	9.0	76	12	12
279.5	3.0	59.7	72	18	11
240.5	19.0	19.2	80	9	11
240.5	26.5	29.9	78	10	11
240.5	42.5	39.1	76	12	11
240.5	66.0	52.1	75	15	11

[a] The first two entries were run at the same time and were identical except that the first entry used 550 mg of sample/10 ml of ampoule (some liquid phase) and the second entry used 20 mg of sample/10 ml of ampoule. All the other entries used 10–20 mg of sample/10 ml of ampoule. [b] At very long times 2–5% of other products are formed which have long retention times on glc.

The rates of reaction were well behaved even when ampoules were intentionally prepared in different ways, although water must be excluded since hydrolysis of the trimethylsilyl group occurs if water is present. The ratio of sample size to ampoule size is relatively unimportant; *viz.*, a sample of 20 mg of **1**-OTMS/10 ml of ampoule and of 66 mg of **1**-OTMS/0.6 ml of ampoule gave identical rates (the latter sample was not all in the gas phase). Kinetic runs were all run at the lower concentration where no liquid phase can be seen at the temperature of reaction. The rate of disappearance of **1**-OTMS showed first-order behavior. Table III presents the variation of rate with temperature and the resulting activation parameters.

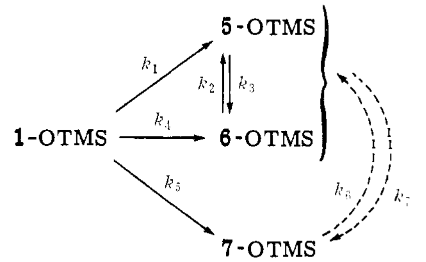
Table III. First-Order Rate of Disappearance of 1-Trimethylsiloxy-1-vinylcyclonon-3-ene (**1-OTMS**)

Temp, °C[a]	10^6k, sec^{-1} [b,c]	Correlation coeff
240.5	3.04 ± 0.02	0.995
261.0	15.7 ± 0.5	0.992
279.5	82.0 ± 0.5	0.992
299.0	345 ± 2	0.997
	E_a = 47.7	0.999
	A = $10^{14.75}$	

[a] Determined by ASTM thermometer in the NaNO$_2$–KNO$_3$ fused salt bath. [b] The rate constant is that obtained by least-squares fit of 10–13 data points for each temperature. The error is the average deviation of those points from the corresponding line. [c] Internal glc standard experiments indicated a material balance of 90% for the pyrolysis–hydrolysis sequence. Duplicate independent rate measurements at 299.0 and at 279.5° differed by less than 5%.

The kinetics of the entire system were treated as the system shown in Scheme I, where k_6 and k_7 were assumed to be negligible.[15] The solved differential equations are shown as eq 5–8. Rate constants k_1, k_4, and

Scheme I. The System of Rate Constants Used in Eq 5–8



$$[\mathbf{1}\text{-OTMS}] = [\mathbf{1}\text{-OTMS}]_0 e^{-(k_1 + k_4 + k_5)t} \quad (5)$$

$$[\mathbf{5}\text{-OTMS}] = \left[\frac{k_2(k_1 + k_4 + k_5) - k_2k_5}{(k_1 + k_4 + k_5)(k_2 + k_3)}\right] \times [\mathbf{1}\text{-OTMS}]_0[1 - e^{-(k_2 + k_3)t}] + \left[\frac{(k_1 - k_2)(k_1 + k_4 + k_5) + k_2k_5}{(k_1 + k_4 + k_5)(k_2 + k_3 - k_1 - k_4 - k_5)}\right] \times [\mathbf{1}\text{-OTMS}]_0[e^{-(k_1 + k_4 + k_5)t} - e^{-(k_2 + k_3)t} \quad (6)$$

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(14) H. O. House, J. L. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, 34, 2324 (1969).

(15) The k_6 and k_7 values may not actually be negligible but the assumption can be used because 7-OTMS is initially generated in nearly the equilibrium concentration (see the long reaction times in Table II). The values for k_2 and k_3 evaluated in this way may contain components in which isomerization takes place *via* 7-OTMS. Derivations of the kinetic expressions will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-7074. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

$$[\mathbf{6}\text{-OTMS}] = \left[\frac{k_3(k_1 + k_4 + k_5) - k_3k_5}{(k_1 + k_4 + k_5)(k_2 + k_3)}\right] \times [\mathbf{1}\text{-OTMS}]_0[1 - e^{-(k_2 + k_3)t}] + \left[\frac{(k_4 - k_3)(k_1 + k_4 + k_5) + k_2k_5}{(k_1 + k_4 + k_5)(k_2 + k_3 - k_1 - k_4 - k_5)}\right] \times [\mathbf{1}\text{-OTMS}]_0[e^{-(k_1 + k_4 + k_5)t} - e^{-(k_2 + k_3)t}] \quad (7)$$

$$[\mathbf{7}\text{-OTMS}] = \frac{k_5[\mathbf{1}\text{-OTMS}]_0}{(k_1 + k_4 + k_5)}[1 - e^{-(k_1 + k_4 + k_5)t} \quad (8)$$

k_5 were estimated from the initial rates and were refined along with k_2 and k_3 using a computer program which was designed to use the system shown in Scheme I (*i.e.*, eq 5–8) to simulate the experimental data.[16] The resultant fit, which has less than 1% average deviation, is shown graphically in Figure 1. The rate constants determined in this way are summarized in Table IV.

Table IV. Rate Constants[16] at 299° Determined by Computer Simulation of the Date Using Eq 5–8

Rate constant	Interconversion	10^6k
k_1	**1**-OTMS ⟶ **5**-OTMS	28.4
k_2	**6**-OTMS ⟶ **5**-OTMS	2.3
k_3	**5**-OTMS ⟶ **6**-OTMS	4.3
k_4	**1**-OTMS ⟶ **6**-OTMS	4.5
k_5	**1**-OTMS ⟶ **7**-OTMS	4.5

The rate constants k_6 and k_7 could be estimated in a similar way;[17] however, the change in concentration of **7**-OTMS is too small for this to be meaningful. It is clear, however, that regardless of the magnitude of k_6 and k_7, the rate constants for cis–trans equilibration *via* **7**-OTMS can be no greater than k_2 and k_3.

Discussion

Thermal Rearrangements of 1-OTMS. Two of the rearrangement products, **5**-OTMS and **7**-OTMS, represent [1,3] and [3,3] sigmatropic shifts which are symmetry allowed (see introduction). The third product, **6**-OTMS, involves both a [1,3] sigmatropic shift and loss of the cis stereochemistry of the double bond not taking part in the rearrangement. This is clearly not a one-step concerted process. Although **5**-OTMS and **6**-OTMS interconvert[18] under the reaction condition, that interconversion is much too slow to account for the formation of **6**-OTMS at very low conversion (see Table II).

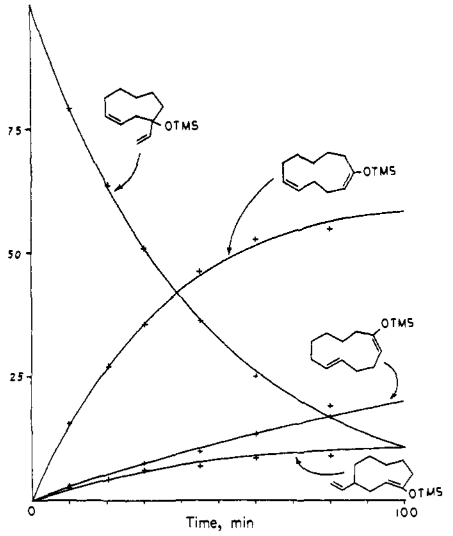
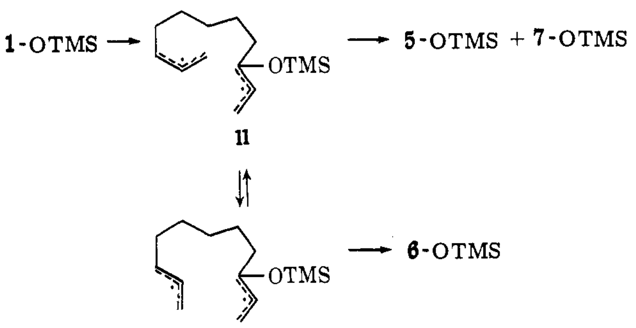


Figure 1. Isomerization of **1**-OTMS at 299°. The crosses represent experimental data. The solid lines correspond to a computer simulation using eq 5–8 and the rate constants shown in Table IV.

Scheme II



One way to accommodate these results would be to postulate that the rearrangement proceeds *via* a diradical **11** that can lead to all three products (Scheme II). The activation parameters are consistent with formation of such an intermediate. The activation energy, 47.7 kcal/mol, agrees with the value predicted from bond dissociation energies[19] and the preexponential term, $10^{14.75}$, is quite similar to other diradical reactions.[5] While the activation parameters are consistent with the intermediacy of the diradical, they do not necessarily exclude concerted paths. One case has been shown to give stereochemistry that indicates a concerted rearrangement but activation parameters consistent with a biradical intermediate.[20]

How reasonable is the postulate that the allylic radical partially loses configuration before undergoing reclosure? The ratio of cis product **5**-OTMS to trans product **6**-OTMS implies that the barrier to reclosure would have to be approximately 3 kcal/mol less than that for stereochemical loss by the allyl radical. The latter should be approximately the same as the allylic resonance energy.[21,22] Measurements by Benson, *et al.*, place that value at 9.6 ± 3 kcal/mol which would then imply a barrier to reclosure of 4–10 kcal/mol.[23] Presumbly the major source of this barrier is the entropy change associated with restricting the motion of **11**

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[16] In general, each rate constant actually represents a combination of processes since 5-OTMS, 6-OTMS, and 7-OTMS are actually mixtures of cis–trans isomers about the enol double bond.

[17] R. A. Alberty and W. G. Miller, *J. Chem. Phys.*, **26**, 1231 (1957).

[18] Both 5-OTMS and 6-OTMS are actually a mixture of cis–trans isomers about the enol double bond. To say that 5-OTMS and 6-OTMS interconvert means that some process allows the stereochemistry of the other double bond to be lost. It should be noted that *cis-* and *trans*-cyclodecene do not interconvert appreciably under these conditions which argues against a simple rotation about the double bond.

[19] This comparison was carried out in the same way as outlined in ref 7.

[20] J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **92**, 1096 (1970); J. A. Berson, Abstracts of the 22nd National Organic Chemistry Symposium of the American Chemical Society, 1971.

[21] K. W. Egger, P. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964).

[22] Although values range between 10 and 25 kcal/mol most values fall near 13 kcal/mol.[21,23] Convincing arguments have been made that "must surely lay to rest any thought that the allylic resonance energy is much greater than 12 kcal/mol."[23]

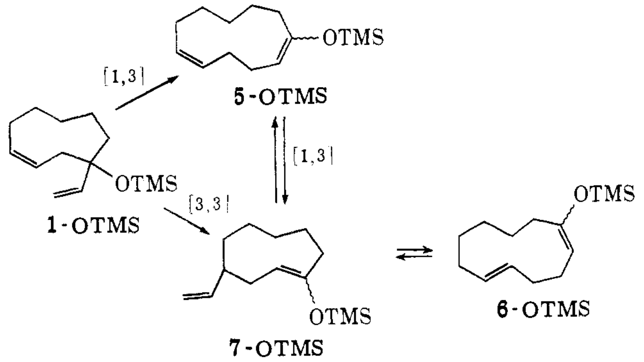
[23] D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, 91, 2136 (1969), and references cited therein.

during reclosure. The 4–10-kcal/mol range does not seem unreasonable since the radical centers that must be combined are separated by seven or nine carbons.

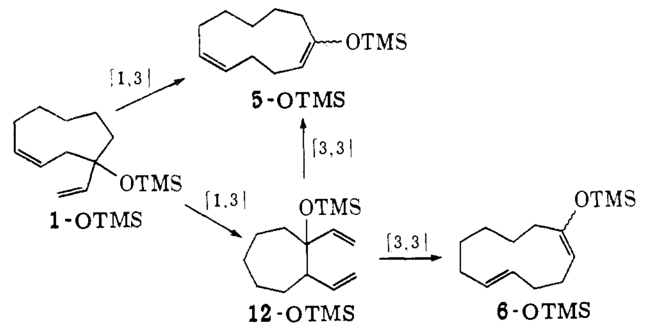
In a more recent study,[24] the barrier for configurational loss in the allyl radical was estimated to be 21 ± 3 kcal/mol. If this unusually high value is accepted, formation of **6**-OTMS by the mechanism shown in Scheme II is unreasonable. The barrier to reclosure would have to be at least 18 kcal/mol which is not compatible with the unsuccessful attempts to trap the diradical in toluene.[25]

The loss of stereochemistry could also occur through sequential rearrangements. In Scheme III, the cis geometry would be lost by passing through **7**-OTMS that could give the trans isomer **6**-OTMS through rotation of the vinyl group. Since **6**-OTMS is found even at very low conversion, the rate of isomerization of **7**-OTMS to form **6**-OTMS would have to be relatively fast. The kinetic data do not support this in that the products do not interconvert rapidly and **7**-OTMS does not disappear as would be required if the process were irreversible.

Scheme III[27]

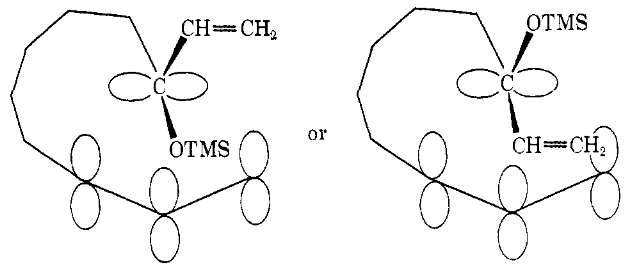


Scheme IV[27]



Scheme IV postulates a ring-contracted product, **12**-OTMS, as an additional higher energy component[28] that is not seen because it is not present in measurable amounts.[33] The divinyl compound, **12**-OTMS, could be formed with the cis or trans stereochemistry, either of which could rearrange to **5**-OTMS or **6**-OTMS. To fit the data **12**-OTMS must be formed at a comparable rate to **5**-OTMS and must rearrange much faster than it is formed. This is not unrealistic inasmuch as [3,3] shifts are often faster than [1,3] shifts. This scheme provides an all-symmetry-allowed pathway to all the products; however, it is unlikely that all the steps are in fact concerted. A concerted [1,3] shift that would generate **12**-OTMS would rotate a very bulky group across the allyl moiety (Chart I). Berson and Nelson have shown that when a methyl group on the migratory carbon must rotate into the allyl moiety, it prevents the concerted [1,3] rearrangement in a case that otherwise appears to undergo concerted rearrangement without that methyl group. Thus the loss of stereochemistry could occur either through **12**-OTMS or by configurational loss in **11** but in either case a biradical intermediate is implicated for at least part of the products. Some of the rearrangements could be concerted but we have no evidence to clearly indicate that they are.

Chart I. Two Transition States for a Concerted [1,3] Sigmatropic Shift Resulting in Ring Contraction



Thermal Rearrangements of 1-OH. The use of hydroxyl, rather than a trimethylsiloxy group, is quite detrimental to the yield of ring-expanded products. This is partly because elimination occurs more readily, such that alkenes normally make up 5–20% of the volatile product. The amount was quite irreproducible which suggests that the elimination and/or subsequent polymerization of the alkenes depends on surface conditions. In addition, β-hydroxy olefin cleavage (eq 4) produces undeca-1,10-dien-3-one (**8**) which polymerizes readily even when stored at room temperature. The product ratio at early time (see Table I) shows that at least 25% of the rearrangement product results from β-hydroxy olefin cleavage. This is a lower limit because the cleavage product **8** is unstable under these conditions as can be seen from the decrease in the ratio of **8**:**5** at longer reaction times. Approximately 60% of the substrate **1**-OH is lost to elimination and cleavage followed by polymerization.

The three ketone products **5**, **6**, and **7** are formed in nearly the same ratio as the initial product ratio from the siloxy-Cope reaction. The ratio of products does not change appreciably with time. This suggests that the enol products convert to the keto forms which do not interconvert appreciably under these reaction conditions. Conversion of the enol to the keto form is energetically favorable by *ca.* 10 kcal/mol;[34] however,

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(24) R. J. Crawford, J. Hamelin, and B. Strehlke, *J. Amer. Chem. Soc.*, **93**, 3810 (1971). The estimate is based on small differences in product mixtures obtained at a single temperature.

(25) Others[26] have trapped diradicals with reclosure barriers estimated to be 14 kcal/mol.

(26) H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 3515 (1969).

(27) Throughout this paper, the trimethyl 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.

(28) The enol portions of **5**, **6**, and **7**-OTMS favor these products relative to **12**-OTMS by 5–7 kcal/mol,[29,30] while ring strain favors **12**-OTMS by only *ca.* 3.5 kcal/mol.[31,32]

(29) G. Pilcher, H. A. Skinner, A. S. Pell, and A. E. Pope, *Trans. Faraday Soc.*, **59**, 316 (1963).

(30) S. J. Rhoads and E. E. Waali, *J. Org. Chem.*, **35**, 3358 (1970).

(31) J. D. Dunitz and V. Prelog, *Angew. Chem.*, **72**, 896 (1960).

(32) Y. I. Gol'dfarb and L. I. Belon'kii, *Russ. Chem. Rev.*, **29**, 214 (1960).

(33) This type of compound is observable in the eight-membered analog.[12]

(34) Estimated by the semiempirical method of Cox.[35]

(35) J. D. Cox, *Tetrahedron*, **19**, 1175 (1963).

this [1,3] hydride shift is not symmetry allowed,[3] which means that the enol–keto interconversion may not be especially fast. This is not inconsistent with our data since a very fast conversion is not necessarily indicated. Furthermore, enol–keto interconversion might occur by a nonconcerted, bimolecular, or surface-catalyzed pathway.

The mechanism of the rearrangement of **1**-OH is probably similar to that for **1**-OTMS except that β-hydroxy olefin cleavage can also take place and ketone formation prevents product interconversion. Although accurate rate measurements could not be made because of the erratic side reactions, the oxy-Cope rearrangements require the same temperature range as the siloxy-Cope rearrangements which suggests a biradical intermediate.

Synthetic Application. From the standpoint of synthetic utility, the siloxy-Cope variation represents a substantial improvement in yield relative to the oxy-Cope method. It successfully prevents the serious β-hydroxy olefin cleavage and elinination side reactions of the oxy-Cope method. A further advantage is that the siloxy-Cope rearrangement need not be run in the gas phase which can be quite inconvenient on a large scale. The present system gave the same rate and products in the gas phase and as a neat liquid. The oxy-Cope substrate polymerized badly as a neat liquid ($<1\%$ yield).

When used as a ring expansion, the overall change in ring strain can be very important. Ring sizes larger than nine-membered should expand, whereas some smaller rings may not. In some cases the formation of ketone from the enol products might be expected to tip the balance such that the oxy-Cope would provide a ring expansion whereas the siloxy-Cope would not. The eight-membered ring is such a case which we shall report in more detail.[12]

One problem with the siloxy-Cope ring expansion is that the stereochemistry of the double bond tends to be lost, increasingly with time, due to product interconversion. This could be used to advantage if one wants both isomers or the more stable isomer. In some cases, *e.g.*, the ten-membered analog,[36] the rate of interconversion is so slow relative to the rate of product formation that high stereochemical integrity can be maintained.

The use of the siloxy group is not restricted to rings. In many open-chain systems where β-hydroxy olefin cleavage is a serious competitor with the oxy-Cope reaction,[6] the siloxy derivative could prevent the cleavage but still provide some driving force *via* the enol form. In cases where the reaction ultimately leads to an aldehyde, the siloxy derivative also protects the aldehyde from decomposition under the reaction conditions. Shortly after our initial report,[1] Corey and Herron provided an interesting application of this type.[37]

Experimental Section

General. Infrared spectra were measured on a Beckman IR 8 infrared spectrometer. Nmr spectra were measured on a Varian Associates A-60 or HA-100 instrument. 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 or Galbraith Laboratories. Boiling points are uncorrected. Analytical gas–liquid chromatography (glc) utilized a Wilkens Aerograph Model 1200 instrument with flame ionization detector which was equipped for either $^1/_8$-in. packed columns or 0.01-in. capillary columns. Preparative glc was done with an Aerograph A-90-P instrument.

***cis*-Cyclonon-3-en-1-ol** was synthesized from cyclooctene in six steps according to the method of Poulter, Friedrich, and Winstein.[8]

***cis*-3-Cyclononenone.** A solution of 260 ml of water, 43 ml of sulfuric acid, and 28.3 g of chromium trioxide was chilled to 0°. After 65 g of manganous sulfate was dissolved in the above solution, 1 l. of reagent acetone was added and the reaction was again chilled to 0°. A solution of 26 g of *cis*-cyclonon-3-en-1-ol in 150-ml of reagent acetone was added over 10 min. After 20 min the reaction was complete (by glc). The inorganic solids were removed by filtration. The aqueous acetone solution was concentrated and extracted into ether solution which was washed with water and saturated sodium bicarbonate (three times). After drying ($MgSO_4$), the solvent was removed and the product was distilled [bp 54–57° (0.1 mm)]. This gave 18.6 g (73%) of clear oil: ir (neat) 3.30, 3.42, 3.48, 5.90, 6.95, 13.35, 13.70 μ; nmr (CS_2, δ) 5.5–5.8 (m, 2), 3.0–3.2 (m, 2), 2.1–2.7 (m, 4), 1.4–2.1 (m, 6).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.09; H, 10.04.

***cis*-1-Vinylcyclonon-3-en-1-ol (1-OH).** The procedure used was similar to that used by Fuson and Mon.[38] A solution of 5.0 g of vinyl bromide in 13 ml of dry THF was added under nitrogen to 8.3 g of magnesium. The flask was warmed until the reaction started and then an additional 81 ml of dry THF was added. A solution of 31 g of vinyl bromide in 68 ml of dry THF was added over 45 min so as to maintain a gentle reflux. The reaction was then heated at 55° for 1.5 hr. The reaction mixture was chilled to 0° and 18 g of *cis*-3-cyclononenone in 50 ml of THF was added over 10 min. After 1 hr the reaction was complete (analyzed by glc) and 100 ml of saturated ammonium chloride solution was added dropwise at 0°. The organic material was extracted into 700 ml of 50:50 ether–pentane which was washed three times with 400 ml of water and finally saturated sodium chloride solution. After drying ($MgSO_4$) and solvent removal, the product was distilled [bp 69–73° (0.1 mm)] which gave 17.0 g (79%) of clear oil: ir (neat) 2.95, 3.30, 3.40, 3.48, 6.10, 10.10, 10.90, 12.75, 13.60 μ; nmr (CCl_4, δ) 5.95, 5.20, 4.97 (ABC pattern, J = 1, 10, and 18 Hz; 3), 5.4–5.7 (m, 2), 2.0–2.5 (m, 4), 1.4–1.8 (m, 8), 1.2 (s, OH). The double bond stereochemistry is 98.7% cis as shown below for the trimethylsilyl derivative.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.28; H, 10.99.

***cis*-1-Methoxy-1-vinylcyclonon-3-ene (1-OCH$_3$).** A mixture of 1 g of alcohol **1-OH**, 12.5 ml of dry THF, and 0.27 g of potassium metal was stirred for 2 hr at room temperature. Then 0.8 ml of methyl iodide was slowly added to the mixture which was cooled with an ice bath. The reaction turned clear orange and then cloudy yellow. The reaction was extracted with pentane and the pentane solution was washed with water and dried over magnesium sulfate. Analysis by glc indicated that 61% of the product was the desired ether, 18% was a mixture of *cis,cis*- and *cis,trans*-4-ethylidenecyclononene (**10**), 12% of starting alcohol, and 9% of five unknown compounds. Separation by glc on a 0.25 in. × 7 ft, 10% diethylene glycol succinate (DEGS) on Chromosorb W column at 110° gave the pure ether: ir (neat) 3.30, 3.40, 3.50, 3.55, 9.25, 9.35, 10.90, 12.75, 13.60; nmr (CCl_4, δ) 5.65, 5.13, 5.02 (ABC pattern, J = 2, 11, and 17 Hz; 3), 5.2–5.7 (m, 2), 3.12 (s, 3), 2.0–2.6 (m, 4), 1.2–1.8 (m, 8).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.12; H, 11.34.

The glc separation also gave a sample of the by-products *cis,cis*- and *cis,trans*-4-ethylidenecyclononene (**10**) which were identified by spectral and glc comparison with authentic material (see below).

***cis,cis*- and *cis,trans*-4-Ethylidenecyclononene (10).** Reaction of *cis*-4-cyclononenone with triphenylphosphonium ethylide[39,40] yields a mixture of *cis,cis*- and *cis,trans*-4-ethylidenecyclononenone (*ca.* 44:56 mixture of the two isomers when analyzed on a 100 ft × 0.01 in. HBMA capillary column): ir (neat) 3.30, 3.40, 3.46, 6.03, 6.80,

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(36) Unpublished work in these laboratories carried out by J. B. Billigmeier.

(37) E. J. Corey and D. K. Herron, *Tetrahedron Lett.*, 1641 (1971).

(38) R. C. Fuson and M. T. Mon, *J. Org. Chem.*, **26**, 756 (1961).

(39) G. Wittig and U. Schollkopf, *Org. Syn.*, 40, 66 (1960), and references cited therein.

(40) This experiment was performed by Y. B. Choi as part of a masters thesis.

6.95, 12.20, 12.43, 12.70, 13.25, 13.68, 14.43; nmr (CS_2, δ) 5.0–6.0 (m, 3), 2.6–2.8 (m, 2), 2.0–2.4 (m, 4), 1.2–1.7 (m, 9).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 88.08; H, 11.87.

***cis*-1-Trimethylsiloxy-1-vinylcyclonon-3-ene (1-OTMS)** was prepared by stirring 2 g of alcohol **1-OH**, 8 ml of DMSO, and 4 ml of Tri-Sil[9] for 30 min at room temperature. The lower DMSO layer was separated and extracted with 80 ml of pentane which was then combined with the original upper layer. The pentane solution was then washed with 80 ml of water, 25 ml of 5% sulfuric acid, and 25 ml of saturated sodium bicarbonate. After drying ($MgSO_4$), the solvent was removed and the material was distilled through a 5-cm Vigreux column [bp 69–73° (0.1 mm)] which gave 2.6 g (90% yield) of a clear oil that was 93% pure as measured by gas chromatography. The cis:trans ratio was 98.7:1.3. Further purification on a 0.25 in. × 7 ft, 5% KOH–5% Carbowax 4000 on 60–80 Chromosorb W gave **1-OTMS** which was pure except for 1.3% of the trans isomer. Samples that were to be examined at low conversions were first purified by preparative thick-layer chromatography using 10% silver nitrate on Silic AR[41] (25% ether–pentane eluent) before glc purification. This gave cis isomer that was totally free of trans within the limits of detection (<0.02% trans): ir (neat) 3.30, 3.48, 6.10, 8.02, 9.30, 9.60, 10.90, 11.95, 13.34, 13.65; nmr (CCl_4, δ) 5.88, 5.08, 4.98 (ABC pattern, J = 1, 10, and 18 Hz; 3), 5.3–5.7 (m, 2) 2.9–3.4 (m, 4), 1.1–1.4 (m, 8), 0.08 (s, 9).

Anal. Calcd for $C_{14}H_{26}O$ Si: C, 70.52; H, 10.91. Found: C, 70.42; H, 11.01.

Cis–Trans Isomerization of 1-OTMS. A solution of 5 mg of **1-OTMS** in 1 ml of benzene was irradiated for 1 hr in a quartz tube in a Rayonet photochemical reactor. This produced an 86:14 mixture of starting **1-OTMS** and a slightly shorter retention-time component that we presume is the trans isomer. Further irradiation for 2 hr changed the ratio to 84:16. The retention time of the short retention-time component agrees with that of a 1.3% contaminant in **1-OTMS** on both 100-ft Apiezon and 125-ft UCON LB550X capillary columns.

Ampoule Thermolysis of 1-OH. Pyrex ampoules were washed with acetone, water, and concentrated ammonium hydroxide. The ampoules were dried at room temperature under 0.1-mm vacuum for at least 30 min. In a typical run, 10 μl of alcohol **1-OH** was injected into a 10-ml ampoule which was then evacuated (0.1 mm) for 25 min and then sealed. The ampoule was placed in an aluminum oven or in a fused salt bath maintained by a Bailey temperature controller.

The ratio of sample size to ampoule size was important. Decreasing the ratio of compound to ampoule size gave more elimination while increasing the ratio gave more polymerization. The elimination reaction was also more pronounced if the ampoules were acid or base washed or if they were not dried completely.

The product mixture was analyzed on 0.01 in. × 75 ft DEGS or UCON LB550X capillary columns and on a $^1/_8$ in. × 30 ft 0.1 Carbowax 1000 on Corning glc 110. The products were isolated by a combination of thick-layer chromatography on Silic AR[41] and gas chromatography on a 0.25 in. × 7 ft, 10% DEGS on 60–80 Chromosorb W and on a 0.25 in. × 17 ft, 10% SF96 70–80 Chromosorb G column using temperatures of 160–185° and a flow of 30 ml/min. This gave the four products below.

Structural Assignment for *cis*-5-Cycloundecenone (5). Hydrogenation of **5** over Adam's catalyst gave cycloundecenone (ir spectra identical with that of an authentic sample from Aldrich Chemical Co.).

A 12-mg sample of **5** was ozonized in 2 ml of dry ethyl acetate while the flask was cooled in a Dry Ice–acetone bath. The ethyl acetate was removed under reduced pressure and replaced with 2 ml of acetone. Jones reagent[42,43] was added until the brown color persisted at which time the product was extracted into ether. The keto diacid product was extracted into 5% sodium bicarbonate which was then acidified. The product was extracted into ether solution and dried ($MgSO_4$). Crystallization from carbon tetrachloride gave a keto diacid, mp 91.5–93°, with nmr and ir spectra identical with the ozonolysis product of 1-(4-pentenyl)cycloheptene (**9**). Compound **9** was prepared by reacting 4-pentenylmagnesium bromide[44] with cycloheptanone followed by dehydration[45] of the resulting tertiary alcohol with phosphorus oxychloride. This gave approximately a 50:50 mixture of two alkenes which were separated by gas chromatography on a 0.25 in. × 7 ft, 5% UCON LB550X on Chromosorb column. Ozonolysis of the appropriate isomer in the same way as above gave a keto diacid which was crystallized from carbon tetrachloride, mp 87–91°. The melting point was not depressed when mixed with keto diacid from **5**.

The spectral properties of **5** are: ir (CS_2) 3.33, 3.40, 3.50, 5.86, 14.40 μ; nmr (CCl_4, δ) 5.2–5.5 (m, 2), 2.0–2.6 (m, 8), 1.3–2.0 (m, 8).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.28; H, 10.99.

Structure Assignment for *trans*-5-Cycloundecenone (6). Hydrogenation of **6** over Adam's catalyst gave cycloundecenone. When the cis isomer **5** was photolyzed in benzene (Rayonet reactor) a 63:37 mixture of **5** and **6** resulted. The spectral properties of **6** are: ir (CS_2) 3.30, 3.40, 3.50, 5.86, 10.25 μ; nmr (CS_2, δ) 4.9–5.2 (m, 2), 1.2–2.3 (m, 16).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.36; H, 10.91. Found: C, 79.33; H, 10.96.

Structure for 4-Vinylcyclononanone (7) has been assigned by analogy with the corresponding product of the next lower homolog of **1-OH** where this type of compound was confirmed by independent synthesis.[12] The spectral properties are also consistent with this structure: ir (CCl_4) 3.40, 3.48, 5.90, 10.96 μ; nmr (CCl_4, δ) 5.70, 4.84, 4.80 (ABC pattern, J = 1, 10, and 16 Hz; 3), 1.2–2.4 (m, 15).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.62; H, 11.03.

Structure for Undeca-1,10-dien-3-one (8) was assigned from the spectral data below: ir (neat) 3.40, 3.50, 5.98, 6.0, 6.20, 7.15, 10.10, 10.43, 11.03 μ; nmr 5.5–6.3 (m, 4), 4.7–5.1 (m, 2), 2.3–2.7 (m, 2), 1.9–2.3 (m, 2), 1.2–1.9 (m, 8); mass spectrum (70 eV) 166 (parent), 83 (19% of base, γ cleavage), 70 (67% of base, McLafferty rearrangement), 55 (base, α cleavage).

Ampoule Thermolysis of 1-OTMS. Pyrex ampoules were prepared, sealed, and heated as above. Unlike the alcohol pyrolyses, these thermolyses were not notably sensitive to the way the ampoules were prepared except that they must be dry. Sample concentrations varied from 5 mg/10 ml of ampoule to 550 mg/10 ml of ampoule and all gave the same rate and products when other conditions were held constant. The products were analyzed before hydrolysis on a 0.01 in. × 75 ft DEGS capillary column.

The crude mixture was hydrolyzed by refluxing 10 mg of sample in 0.5 ml of a solution consisting of 10 ml of pyridine, 1 ml of water, and 2 drops of concentrated hydrochloric acid.[46] The sample was extracted into 5 ml of ether which was washed three times with 5 ml of 10% sulfuric acid and once with saturated sodium bicarbonate and then dried over magnesium sulfate. The products were analyzed and isolated in the same way as for the **1-OH** thermolyses (see above). The products were the same except that **8** was not formed.

Toluene and Cumene Pyrolyses. Ampoules were prepared as above and charged with 10 mg of **1-OTMS** and 0.5 ml of toluene[47] or 0.5 ml of cumene and heated at 296° for 1 hr. The products were analyzed as above and by a glc-mass spectrometer combination. The product ratio was the same as without added toluene or cumene. No products corresponding to trapped biradical were detected.

Kinetic Experiments. A series of 10-ml ampoules was introduced into a fused salt bath which was maintained by a Bailey Model 124 proportional controller. A zero point was removed after 10–30 min and other points were removed and quenched by cooling in a blower. Each ampoule was analyzed as above. The log of the ratio of **1-OH** over the sum of **1-OH**, **5**, **6**, and **7** was plotted *vs.* time.

Acknowledgment. We appreciate the support of this work by the Research Corporation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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[43] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

[44] P. Gaubert, R. P. Linstead, and H. N. Rydon, *ibid.*, 1971 (1937).

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

[47] High pressure is generated under these conditions. One ampoule exploded when 1 ml of toluene was used.