(+)-*endo*-6-Methoxycarbonylbicyclo[2.2.1]heptan-2-one (30). A solution of 29 g of iodine and 112 g of potassium iodide in 340 ml of water was added to a solution of 15.0 g of (+) carboxylic acid **29** in 680 ml of 0.5 N aqueous sodium bicarbonate solution. The mixture was kept overnight at room temperature and then extracted with chloroform. The extract was washed with aqueous sodium thiosulfate, aqueous sodium bicarbonate, and water, and was dried over magnesium sulfate. Evaporation of the solvent gave 25.0 g of **31** (86%), to which 500 ml of 10% aqueous sodium hydroxide solution was added. The mixture was boiled for 1 h and then cooled with ice. After extraction with chloroform, the extract was washed with aqueous sodium thiosulfate and water, and was dried over magnesium sulfate. After evaporation of the solvent, the residue was distilled to give 4.40 g of *endo*-6-carboxybicyclo[2.2.1]heptan-2-one: bp 170–172 °C (5 mm); $[\alpha]^{13}\text{D}$ +16.2° (*c* 0.63, ethanol). The carboxylic acid was treated with a solution of diazomethane in ether by the usual manner. Distillation of the product yielded 4.40 g of **30** (24%): bp 144–146 °C (20 mm); $[\alpha]^{15}\text{D}$ +14.1° (*c* 1.15, ethanol); ir (film) 1750, 1735, 1220, 1195, and 1175 cm^{-1}.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.09; H, 7.27.

(−)-*endo*-6-Hydroxymethylbicyclo[2.2.1]heptan-2-ol (32). A solution of 3.97 g of (+) keto ester **30** in 50 ml of dry ether was added to a suspension of 0.95 g of lithium aluminum hydride in 50 ml of dry ether, and the mixture was refluxed for 4 h. After cooling with ice, saturated aqueous ammonium chloride solution was added to the chilled mixture and inorganic solid was filtered off. The filtrate was washed with water and dried over magnesium sulfate. After removal of the solvent, the residue was distilled to give 2.51 g of **32** (75%): bp 147 °C (5 mm); $[\alpha]^{15}\text{D}$ −1.05° (*c* 0.72, ethanol); ir (film) 3300, 1120, 1045, and 1030 cm^{-1}.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.58; H, 10.05.

(−)-2-Oxatricyclo[4.2.1.0^{4,8}]nonane (8). A solution of 1.02 g of (−) diol **32** in 5 ml of dry pyridine was mixed with 1.36 g of *p*-toluenesulfonyl chloride at 0–5 °C. After stirring for 2 h at this temperature and keeping overnight at room temperature, the solution was poured onto ice and acidified with hydrochloric acid. After extraction with ether, the extract was washed with dilute hydrochloric acid, saturated aqueous sodium bicarbonate, and water, and was dried over magnesium sulfate. Removal of the solvent gave an oily product on which pentane was added. After an immiscible substance was discarded, the solution was concentrated to give a wax. This was sublimed at 70–80 °C (5 mm) to yield 220 mg of **8** (25%): mp 117–119 °C (in a sealed tube); $[\alpha]^{15}\text{D}$ −31.7° (*c* 1.15, ethanol); ir (Nujol) 1145, 1130, 1080, 1040, 1005, 990, 948, 888, and 800 cm^{-1}; NMR ($CDCl_3$) δ 1.0–1.5 (m, 4 H), 1.5–2.0 (m, 2 H), 2.05–2.40 (m, 2 H), 2.50–2.70 (m, 1 H), 3.65–3.90 (m, 2 H), and 4.20–4.42 (m, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.66; H, 9.65.

Registry No.—**7**, 58001-92-6; **8**, 58001-93-7; **10**, 58001-94-8; **11**, 22398-42-1; **14**, 20507-53-3; **15**, 42070-82-6; **16**, 13307-34-1; **17**, 58001-95-9; **18**, 58001-96-0; **19**, 57969-19-4; **20**, 57969-20-7; **21**, 57969-21-8; **22**, 13307-39-6; **23**, 58001-97-1; **24**, 58001-98-2; **25**, 57969-22-9; **26**, 57969-23-0; **27**, 57969-24-1; **29**, 58001-99-3; **30**, 57969-25-2; **32**, 933-91-5; *endo*-6-carboxybicyclo[2.2.1]heptan-2-one, 58002-00-9.

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Thermal Rearrangements of *trans*-1-Trimethylsiloxy-1-vinylcyclotridec-3-ene

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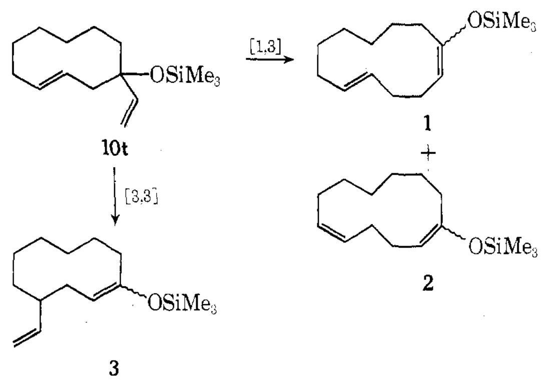
The thermal rearrangement of *trans*-1-trimethylsiloxy-1-vinylcyclotridec-3-ene (**13t**), followed by hydrolysis of the enol ethers, gives two products in comparable amounts: the [1,3] shift ring-expanded ketone, *trans*-cyclopentadec-5-en-1-one (**15t**), and the [3,3] shift product, 4-vinylcyclotridecanone (**14**). Unlike the earlier medium-sized systems, the ratio of [1,3] shift to [3,3] shift product varies with temperature. The activation parameters for the [1,3] shift compare reasonably with similar systems while those for the [3,3] shift are intermediate between the medium-sized ring cases and open-chain systems.

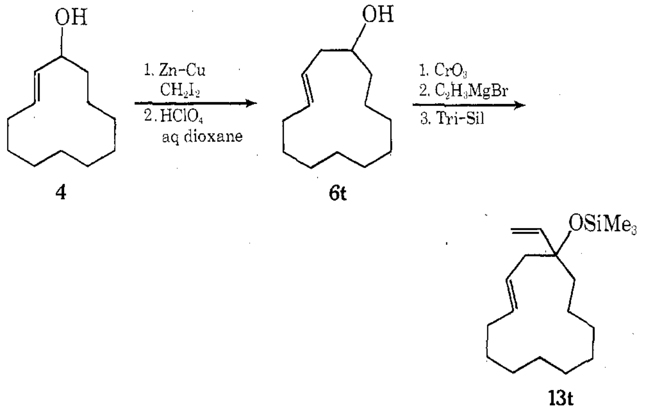
Previous papers in this series[1–3] have described the thermal rearrangements of a set of compounds exemplified by structure **10t**. The major pathway (>70%) for **10t** and for two analogues, the cis isomer, **10c**, and for the cis nine-membered-ring case, **9c**, is a [1,3] sigmatropic shift ring expansion with retention of the ring double bond stereochemistry (e.g., **1**). The [3,3] shift product (e.g., **3**) and the [1,3] shift product with double bond isomerization (e.g., **2**) are formed in minor amounts. The cis eight-membered case, **8c**, is more complex, in that the kinetically preferred pathway is a [1,3] sigmatropic shift ring contraction leading to 1-trimethylsiloxy-1,2-divinylcyclohexane which can then



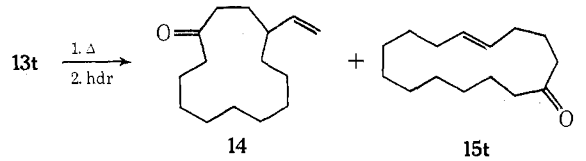
interconvert with the ten-membered ring products that are analogous to **1** and **2**. The present work was carried out to determine whether the same type of two-carbon ring expansion is feasible for large ring systems. Such systems have less ring strain to be released which could result in a higher activation energy which in turn could allow other side reactions to compete.[3]

Results

Preparation of *trans*-1-Trimethylsiloxy-1-vinylcyclotridec-3-ene (13t). A mixture of *cis*- and *trans*-cyclododecene was converted to cyclododec-2-en-1-ol (**4**) by methods described previously.[4] Conversion of **4** to the title compound, **13t**, used the same steps as were used for the ten-membered ring analogue.[3] Only one isomer (trans by infrared) was observable by gas-liquid chromatography (GLC) for **6t** or **13t**. Photolysis of **6t** or **13t** produced in each case another isomer with somewhat longer retention time which was assumed to be the cis isomer.



Thermolysis of 13t. Heating **13t** in evacuated sealed ampules (10 mg of **13t** per 10 ml ampule) at 246–299 °C gave a smooth conversion to a mixture of rearranged trimethylsilyl ethers which hydrolyzed to *trans*-cyclopentadec-5-en-1-one (**15t**) and 4-vinylcyclotridecanone (**14**). The



structures of **14** and **15t** were assigned from their spectral data, especially the NMR spectra which were spread apart using europium shift reagent, Eu(fod)$_3$. Decoupling experiments were then performed to show that there were two methylene groups between the vinyl moiety and the carbonyl for **14** and three methylenes between the double bond and the carbonyl for **15t**. The trans nature of the double bond is evident from the infrared spectrum (970 cm^{-1}).[5,6] *Unlike all previous systems studied, the* [3,3] *shift* product **14t** was dominant and the ratio of **15t** to **14** was temperature dependent (Table I). That ratio did not change measurably during the time required for the kinetic measurements but the product enol ethers do slowly interconvert. This was shown by heating four samples to 90% conversion at 246 °C which gave a 72:28 ratio for **14**:**15t** and then heating three of the samples for times up to 19 h at 289.1 °C at which time the **14**:**15t** ratio was 58:42. The rate of interconversion was estimated to be about tenfold less than the rate of conversion of **13t**.

Table I. First-Order Rate of Disappearance and Product Ratio for 13t

Temp, °C[a]	14/(15 + 14)	$10^5 k$[b]	Corr coeff
246.0	72.0 ± 0.7	0.70 ± 0.05	0.977
254.1	69 ± 1.6	1.34 ± 0.08	0.984
284.4	60 ± 1.5	13.3 ± 0.6	0.992
298.6	54 ± 0.4	39.0 ± 0.5	0.998
	Log *A*	E_a	Corr coeff
Total	13.7	44.9	0.9999
13t → 15t	15.5	50.3	0.9999
13t → 14	12.3	41.8	0.9999

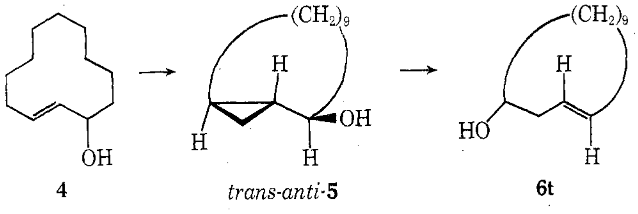
[a] Determined by a platinum resistance thermometer in a NaNO$_2$–KNO$_3$ fused salt bath. [b] The rate constant is that obtained by a least-squares fit of seven to nine data points for each temperature. Internal GLC standard experiments indicated a material balance of 85% for the pyrolysis–hydrolysis sequence. Duplicate independent rate measurements differed by less than 10%.

No cis isomer of **15** (**15c**) was observable under normal GLC conditions. When **15t** was reduced to the alcohol and photolyzed a second peak with somewhat longer retention time was readily observable. Oxidation back to **15** then showed **15t** and a shoulder presumed to be **15c** when optimum GLC conditions were used. Analysis of the pyrolysis samples either as the ketones or reduced to the alcohols indicated that little if any (<2%) **15c** is formed during the first 2 half-lives of reaction of **13t**. At much longer reaction times a small peak for **15c** was observed.

The rate of conversion of **13t** to **14** and **15t** was measured at four temperatures with the results shown in Table I. Good first-order behavior was observed.

Discussion

The synthesis of **13t** follows previous procedures[3,4] but the acid-catalyzed rearrangement of the cyclopropyl alcohol, **5**, is still of special interest because no large-ring or trans-fused examples have been reported. Since only the trans isomer of **6** was formed the stereochemical pattern is presumably the same as for the cis medium-sized ring systems already studied.[1–4,7,8] The Simmons–Smith reaction must be directed to give the anti isomer,[7] *trans-anti*-**5**, which then rearranges with high stereoselectivity to the trans product **6t**. We were not able to detect any cis isomer of **4**, but if it were present it must give the *cis-anti*-**5** which would also rearrange to form **6t**.



The most prominent difference between the thermolysis of **13t** and that of the medium-sized ring analogues is that approximately half of the reaction leads to the [3,3] shift

Table II. Activation Parameters for Siloxy-Cope Rearrangements[a]

	[1,3] shift		[3,3] shift	
	E_a, kcal/mol	Log A	E_a, kcal/mol	Log A
8c	53.9	15.9	53.9	15.0
9c	47.7	14.7	47.7	13.8
10c	50.9	15.8	50.9	14.9
10t	45.1	14.2	45.1	13.3
13t	50.3	15.5	41.8	12.3

[a] Derived from earlier data assuming two competitive first-order processes.

product, **14**, whereas the medium-ring systems gave less than 15% of the [3,3] product. The small percentage formed in the medium-sized ring systems probably reflects a considerable resistance to forming either a chair or boat transition state, either of which bring the vinyl group into the crowded center of the medium-sized ring. The large ring is much more flexible so that the chair (or boat) arrangement is much more attainable. The preexponential value measured for the [3,3] shift process ($10^{12.3}$) is similar to those for other concerted Cope rearrangements (10^{10}–10^{12})[9–11] strongly suggesting a concerted path. The activation energy is considerably higher than normal (41.8 vs. 26–36 kcal/mol)[9–11] but is lower than that measured for the "boat" (44.7 kcal/mol),[9] thus suggesting a chair transition state that still encounters some resistance from the ring.

The above analysis of the [3,3] shift parameters presupposes that the [3,3] and [1,3] shift processes are competing parallel first-order reactions. The mechanistic alternative that both products arise from a common diradical cannot be rigorously excluded. The [1,3] and [3,3] activation parameters are derived from rates of product formation and thus could represent different transition states leading from the diradical to products. In principle the two competing pathways should show a small curvature in the Arrhenius plot for total disappearance of **13t**. A small curvature in the correct direction is in fact observed but the error limits are too great to be certain that the curvature is real.

It is interesting to compare **13t** with the medium-sized ring systems, **9c, 10c,** and **10t,** where the [1,3] to [3,3] product ratio was not measurably temperature dependent (see Table II). For those systems, either both [1,3] and [3,3] shift products arise from a common intermediate or the activation parameters for the two parallel pathways must fortuitously give that impression. That could only happen if the parameters for the [3,3] shift process are somewhat different for **9c, 10c,** and **10t** than for **13t;** in particular the preexponential term must be somewhat larger (ca. 10^{14} vs. 10^{12}) which generally indicates a less ordered transition state.[12] Still it is not inconceivable that the medium ring [3,3] shifts could be concerted since the chair vs. "boat" pathways for 1,5-hexadiene show a 100-fold larger preexponential term for the higher activation energy process which must still be concerted.[9]

The [1,3] shift activation parameters are similar to those observed earlier for the medium-sized ring systems. The magnitude of these activation parameters suggests a diradical; however, earlier stereochemical studies[13,14] have shown that the activation parameters for certain concerted [1,3] shifts are essentially the same as those predicted for a diradical. It has further been argued on theoretical grounds[13] that the diradical should be less favored than the concerted path even if that path is "forbidden concerted", i.e., $[_{\pi}2_s + {}_{\sigma}2_s]$.[13,15] The present results provide little evidence for or against concertedness but they do provide an estimate of the extent to which ring strain is released in the transition state regardless of mechanism. A straightforward comparison can be made with **10t** which only differs in ring size. The **13t** system has approximately 8 kcal/mol less ring strain[17] than **10t** and exhibits an activation energy which is about 5 kcal/mol greater than that for **10t.** This indicates that about 60% ($^5/_8$) of the ring strain is lost in the transition state if one assumes no ring strain in a diradical intermediate or if one assumes that the process is concerted and that the products from **13t** and **10t** have approximately the same ring strain. The latter assumption seems reasonable since saturated large rings have very little ring strain (no data is known for the unsaturated cases).

One further point of interest is the stereochemistry of the ring double bond in the ring expanded product. Retention of stereochemistry for **13t** is complete within the limits of measurement. The medium-sized ring systems, **10t, 10c, 9c,** and **8c,** exhibited loss of stereochemistry of approximately 6, 14, 14, and 35%, respectively. The heavy loss of stereochemistry for **8c** was traced to a very favorable [1,3] shift ring contraction to the six-membered ring divinyl compound which can use a facile [3,3] shift to give both cis and trans products. That process should be somewhat less favorable for **9c, 10c,** and **10t** which would contract to seven- or eight-membered divinyl compounds which would have considerably more strain than the six-membered one. Contraction of **13t** to an 11-membered-ring divinyl compound would be still less favorable, thus providing a reasonable explanation for the lack of cis product **13c.**

Experimental Section

General. Spectral measurements utilized Beckman IR-8, Varian Associates HA100, Atlas CH7, and CEC 110B instruments.[18] Analytical gas–liquid chromatography (GLC) used a Varian Aerograph Model 1200 instrument with the following columns: (A) 0.01 in. × 25 ft UCON LB 550X capillary; (B) 0.125 in. × 10 ft 10% DEGS on 60/80 Chromosorb W; (C) 0.01 in. × 50 ft DEGS PLOT[19] capillary.

***trans*-Cyclododec-2-en-1-ol (4)** was prepared in 31% yield from technical grade cyclododecene by the NBS-solvolysis method described earlier.[4] The spectra agree with those published.[6]

Bicyclo[10.1.0]tridecan-2-ol (5). A mixture of 18 g of zinc–copper couple,[20] 23 g of methylene iodide, 60 ml of anhydrous ether, and a crystal of iodine were stirred under nitrogen while heating with an oil bath at 50 °C. Once the violet color of the zinc–copper couple had formed, 20.7 g of alcohol **4** in 65 ml of anhydrous ether was added in 2 min without the reaction becoming vigorous. A second portion of methylene iodide (45 g) in 20 ml of anhydrous ether was added over 15 min. Analysis of the reaction mixture by GLC (column A, 100 °C) indicated complete reaction 8 h after final addition of methylene iodide. The flask was allowed to cool and the reaction mixture was quenched with saturated ammonium chloride solution. The reaction mixture was vacuum filtered through Celite, which was then washed with ether. The ether layer was dried ($MgSO_4$) and concentrated. The product was purified by liquid chromatography on SilicAR to yield a low-melting white solid (11.5 g, 52%): ir (CCl_4) 3670, 3525, 3070, 3050, 1460, 1455, 1075, 1025, 985 cm^{-1}; NMR (CCl_4) δ 0.1–1.0 (m, 4 H), 1.0–2.3 (m, 19 H), 2.5–2.9 (m, 1 H); mass spectrum, a good analysis was not attainable because no parent peak could be found, but a P − 18 was found at the proper mass.

***trans*-Cyclotridec-3-en-1-ol (6t).** A 20.5-g sample of alcohol **5**, 150 ml of 0.12 M perchloric acid, and 585 ml of dioxane were added to a 2-l. round-bottom flask, equipped with condensor and magnetic stirrer. The solution was heated, with stirring, to 85 °C. The reaction was complete after 3 h (column A, 85 °C). The reaction solution was poured into 3 l. of 50:50 ether–pentane and 150 ml of water. The organic layer was washed once with a saturated sodium bicarbonate solution and once with saturated brine solution, and then dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue, upon cooling, was a low-melting white wax (20.5 g): ir (CCl_4) 3400, 1700, 1460, 1445, 973 cm^{-1}; NMR (CCl_4) δ 1.1–1.5 (m, 16 H), 1.6 (s, 1 H), 1.8–2.4 (m, 4 H), 3.4–3.8 (m, 1 H), 5.2–5.5 (m, 2 H); mass spectrum *m/e* 196.181 (calcd for $C_{13}H_{24}O$, *m/e* 196.183).

***trans*-Cyclotridec-3-en-1-one (7).** A 9.49-g sample (120 mmol) of dry pyridine and 150 ml of methylene chloride were combined. To this solution was added 6.00 g (60 mmol) of chromium trioxide with stirring.[21] After 15 min, 1.96 g (10 mmol) of **6t** was added in a small amount of methylene chloride. A tarry, black deposit separated immediately. The reaction mixture was allowed to stir for an additional 15 min before 50 ml of anhydrous ether was added to coagulate the chromium salts. The mixture was gravity filtered, and the residue washed with 200 ml of anhydrous ether. The two organic phases were combined and washed three times with 100-ml portions of 5% aqueous sodium hydroxide, once with a 100-ml portion of 5% aqueous hydrochloric acid, once with a 10-ml portion of aqueous sodium bicarbonate, once with a 100-ml portion of saturated copper sulfate, and once with a 100-ml portion of saturated brine solution. The product was dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated. This oil was taken on to the next reaction without further purification (crude yield 100%): ir (neat) 1710, 1460, 1455, 1360, 972 cm^{-1}; NMR (CCl_4) δ 1.0–1.9 (m, 14 H), 1.9–2.2 (m, 2 H), 2.2–2.5 (t, 2 H), 2.8–3.1 (d, 2 H), 5.3–5.6 (m, 2 H); mass spectrum *m/e* 194.167 (calcd for $C_{13}H_{22}O$, *m/e* 194.168).

***trans*-1-Vinylcyclotridec-3-en-1-ol (8).** A 5.7-g (0.029 mol) sample of **7** was treated with vinylmagnesium bromide as described earlier[1] which gave 5.9 g (91%) of a viscous yellow oil: ir (neat) 3450, 3125, 1640, 1460, 1445, 1420, 1125, 1070, 980 cm^{-1}; NMR (CCl_4) δ 1.0–1.7 (m, 16 H), 1.7–2.1 (m, 2 H), 2.1–2.2 (d, 2 H), 2.4–2.6 (s, 1 H), 4.8–6.3 (m, 5 H); mass spectrum *m/e* 222.198 (calcd for $C_{15}H_{26}O$, *m/e* 222.198).

***trans*-1-Trimethylsiloxy-1-vinylcyclotridec-3-ene (13t).** This compound was prepared from **8** by the procedure outlined earlier.[1] The product was vacuum transferred at 0.25 mm in an Aldrich Kugelrohr apparatus (100 °C air bath) to give **13t:** ir (CCl_4) 3110, 1455, 1415, 1225, 1055, 975, 920, 835 cm^{-1}; NMR (CCl_4) δ 0.9–1.7 (m, 16 H), 1.7–2.1 (m, 2 H), 2.1–2.3 (d, 2 H), 2.4 (s, 10 H), 4.8–6.3 (m, 5 H); mass spectrum *m/e* 294.230 (calcd for $C_{15}H_{34}OSi$, *m/e* 294.237).

Ampule Pyrolysis of *trans*-1-Trimethylsiloxy-1-vinylcyclotridec-3-ene (13t). Pyrex ampules (10 ml) were washed with acetone, water, and concentrated ammonium hydroxide, then dried overnight at 120 °C in an oven. In a typical analytical run, a 10-μl sample was added to an ampule, which was then evacuated at 0.1 mm for 30 min and sealed. The ampule was placed in an aluminum block oven maintained by a ProportionNul temperature controller or in a fused salt bath maintained by a Bailey temperature controller. The above procedure was also used with larger ampules (65 and 250 ml) using proportionately larger sample sizes. Unlike most earlier systems, higher ratios of compound to ampule size gave decreased yields. The reaction mixture was hydrolyzed as before[1] and analyzed on columns B or C. It was found that under some conditions partial hydrolysis occurred spontaneously during pyrolysis.

Structural Assignment for 4-Vinylcyclotridecanone (14). The structure was assigned by spectral properties: ir (CCl_4) 3110, 1790, 1709, 1645, 1460, 1440, 1350, 1250, 1220, 905 cm^{-1}; NMR (CCl_4) δ 1.1–1.4 (m, 14 H), 1.4–1.8 (m, 4 H), 1.8–2.2 (m, 1 H), 2.3–2.5 (m, 4 H), 4.9–5.8 (m, 3 H); mass spectrum *m/e* 222.196 (calcd for $C_{15}H_{26}O$, *m/e* (222.198). Europium shift studies combined with decoupling experiments support the assignment of the vinyl group to the 4 position.

Structural Assignment for Cyclopentadec-5-en-1-one (15t). The structure was assigned by spectral properties: ir (CCl_4) 1790, 1709, 1455, 1365, 1215, 970 cm^{-1}; NMR (CCl_4) δ 1.1–1.5 (m, 12 H), 1.5–1.8 (m, 4 H), 1.8–2.2 (m, 4 H), 2.2–2.5 (m, 4 H), 5.2–5.4 (m, 2 H); mass spectrum *m/e* 222.196 (calcd for $C_{15}H_{26}O$, *m/e* 222.198). Europium shift studies combined with decoupling experiments support the assignment of the double bond to the 5 position.

Photolysis of *trans*-Trimethylsiloxycyclotridec-3-ene (4-TMS). A solution of 100 mg of **4**-TMS in 10 ml of benzene was irradiated for 1 h in a quartz tube in a Rayonet photochemical reactor. After hydrolysis as above, this produced ca. a 70:30 mixture of **4** and a slightly longer retention time component, which we presume to be the cis isomer (column A, 110 °C).

Photolysis of 13t. A solution of 10 μl of **13t** in 2 ml of benzene was irradiated for 1 h as above. This produced an 87:13 mixture of **13t** and a slightly longer retention time component which we presume to be the cis isomer (column C, 135 °C).

Photolysis of 15t. Ketone **15t** was reduced with lithium aluminum hydride to cyclopentadec-5-en-1-ol. A 20-mg sample was photolyzed in benzene for 50 min. This produced ca. an 87:13 mixture of the starting alcohol and a slightly longer retention time component which we presume to be the cis isomer (column C, 135 °C).

Kinetic Experiments. A series of 10-ml ampules were introduced into a $NaNO_2$–KNO_3 fused salt bath which was maintained by a Bailey Model 124 proportional controller. Ampules were removed at appropriate intervals and quenched in the draft of a fume hood. Each ampule was hydrolyzed and analyzed on column C. The logarithm of the ratio of the alcohol **13t** over the sum of **13t**, **14**, and **15t** was plotted vs. time and analyzed by least squares.

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Registry No.—**4**, 6221-49-4; **4**-TMS, 57969-12-7; **5**, 50991-38-3; **6t**, 57969-13-8; **7**, 57969-14-9; **8**, 57969-15-0; **13t**, 57969-16-1; **14**, 57969-17-2; **15t**, 57969-18-3.

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