(20) I am indebted to a reviewer for pointing out that decarboxylation of **6** should give predominantly *trans*-**15** and that Cope rearrangement would not proceed from *trans*-**15** to **13**, but through a ring-opening reaction prior to decarboxylation. These predictions were amply demonstrated by experiment.
(21) J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry", 3rd ed, McGraw-Hill, New York, N.Y., 1970, p 535.
(22) H. Henecka, Houben-Weyl, "Methoden der Organischen Chemie", Band VIII, Sauerstoff Verbindungen III, Georg Thieme Verlag, Stuttgart, 1952, p 490.
(23) R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 580 (1933).
(24) R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 1995 (1934).
(25) G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3052 (1953).
(26) "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1946, p 250.
(27) See paragraph at end of paper regarding supplementary material.

# Thermal Rearrangement of Trimethylsilyl Enol Ethers of Cyclopropyl Methyl Ketones. A Cyclopentanone Annelation Procedure[1]

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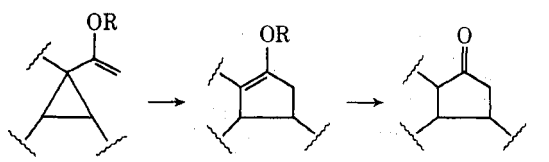
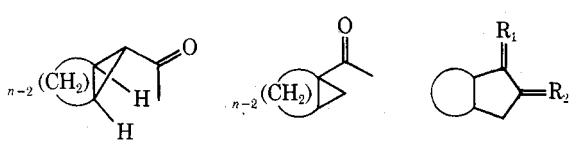
Pyrolysis of the conjugated enol trimethylsilyl ethers derived from methyl cyclopropyl ketone and methyl bicyclo[*n*.1.0]alkan-1-yl ketones (*n* = 3, 4, 5) at 450° yielded, after acidic hydrolysis of the resulting cyclopentene enol silanes, cyclopentanone (73%), bicyclo[3.3.0]octan-2-one (21%), bicyclo[4.3.0]nonan-7-one (99%), and bicyclo[5.3.0]decan-8-one (85%). Rearrangement of the enol silyl ether of methyl *exo*-bicyclo[4.1.0]heptan-7-yl ketone furnished a 1:2 mixture of *cis*- and *trans*-bicyclo[4.3.0]nonan-8-one (52%) and the γ,δ-unsaturated ketone, 2-cyclohexenylacetone (28%). The major products obtained from the enol silyl derivatives of methyl *exo*-bicyclo[3.1.0]hexan-6-yl and methyl *exo*-bicyclo[5.1.0]octan-8-yl ketones were the corresponding γ,δ-unsaturated ketones. This enol silane vinylcyclopropane–cyclopentene rearrangment pathway results in the regioselective annelation of a cyclopentanone ring onto an α,β-unsaturated ketone or an olefin. This overall process furnishes 1-hydroindanone and 1-hydroazulenone in good yields.

The occurrence of five-membered rings in an increasing number of natural products of biological importance has stimulated the development of a variety of new cyclopentane ring synthesis methods. These recent approaches include intramolecular ring closure of acyclic precursors,[2] formal [3 + 2][3] and [4 + 1][4] cycloaddition reactions, and ring contraction[5] and expansion[6] of cyclic substrates. In considering the various general routes to cyclopentanoid ring construction, it appeared to us that the well-established thermal vinylcyclopropane–cyclopentene rearrangement[7] could serve as the basis of a five-membered ring synthesis method in which the newly constructed ring contained a masked ketone functionality. In a general sense, rearrangement of conjugated cyclopropyl enol ethers of part structure **1** would yield cyclopentene enol derivatives **2**. Unmasking of the latent ketone functionality by acidic hydrolysis would then complete the sequence to give the cyclopentanone ring skeleton (eq 1). In particular, thermal



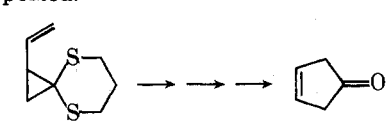
(1)

**1** **2**

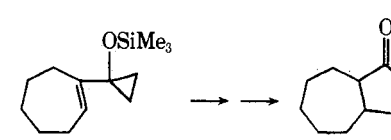


**3a**, *n* = 5 **4a**, *n* = 5 **5**, $R_1 = H_2$; $R_2 = O$
**b**, *n* = 6 **b**, *n* = 6 **6**, $R_1 = O$; $R_2 = H_2$
**c**, *n* = 7 **c**, *n* = 7

rearrangement of the enol derivatives derived from cyclopropyl methyl ketones **3** and **4** would furnish cyclopentanone **5** and **6** regioselectively. Since the cyclopropyl ketone substrates are readily prepared from olefin or α,β-unsaturated ketone precursors, the overall transformation constitutes a net cycloaddition of a one- or a three-carbon atom unit to an existing skeleton to give an annelated cyclopentanone. We have undertaken an examination of the thermal behavior of a series of cyclopropyl enol trimethylsilyl ethers (**1**, R = $SiMe_3$) and the results of this study are detailed below. During the course of our investigation two cyclopentanone ring synthesis methods based on the thermal vinylcyclopropane–cyclopentene rearrangement (eq 2[4a] and 3[6]) were reported.



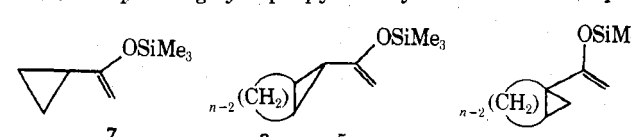
(2)



(3)

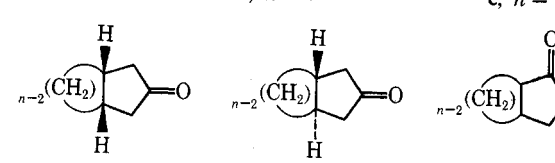
## Results

The specific vinylcyclopropane substrates examined in this study, the parent trimethylsilyl enol ether **7**, and the two bicyclo[*n*.1.0]alkane series **8** and **9**, were prepared from the corresponding cyclopropyl methyl ketones under equil-



**7**

**8a**, *n* = 5 **9a**, *n* = 5
**b**, *n* = 6 **b**, *n* = 6
**c**, *n* = 7 **c**, *n* = 7



**10a**, *n* = 5 **11a**, *n* = 5 **12a**, *n* = 5
**b**, *n* = 6 **b**, *n* = 6 **b**, *n* = 6
**c**, *n* = 7 **c**, *n* = 7 **c**, *n* = 7

**Table I**
**Thermal Rearrangement of Cyclopropyl Trimethylsilyl Enol Ethers[a]**

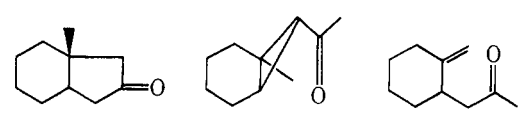
| Substrate | Products (% yield)[b] |
|---|---|
| 7 | Cyclopentanone (73) |
| 8a | **10a** (8), **11a** (3), **13a** (71)[c] |
| 8b | **10b** (17), **11b** (35), **13b** (28) |
| 8c | **10c** + **11c** (5),[d] **13c** (80) |
| 14 | **16a** (64), **15a** + **16b** (7),[d] **15b** (7) |
| 9a | **12a** (21)[e] |
| 9b | **12b** (99) |
| 9c | **12c** (85) |

[a] See text for reaction conditions. [b] Yields determined by VPC using an internal standard and corrected for recovered starting material. [c] An unidentified product (ca. 10%) was also formed. [d] Both isomers present but not separated cleanly. [e] Extensive decomposition was observed.

ibrating conditions ($Me_3SiCl$, $Et_3N$, DMF)[8] or, more conveniently, by kinetic enolate generation (lithium diisopropylamide, THF) followed by quenching with trimethylsilyl chloride.[8] Both methods results in regioselective formation[9] of the conjugated vinylcyclopropane enol silanes **7**, **8**, and **9**. The exo ketones **3** were prepared from the appropriate cycloalkene by the following sequence: copper sulfate catalyzed addition of ethyl diazoacetate, hydrolysis and separation of the exo carboxylic acid by crystallization, and then treatment with methyllithium.[10] The bridgehead substituted ketones **4** were obtained by dimethyloxosulfonium methylide addition to the corresponding $\alpha,\beta$-unsaturated ketones.[11] Attempted thermal rearrangement of enol silane **7** by passing a pentane solution through a conditioned[6] hot tube packed with glass helices at ca. 520° gave, after hydrolysis, substantial amounts of recovered cyclopropyl methyl ketone as well as the desired rearrangement product, cyclopentanone. Satisfactory conversion to products was obtained, however, when the vinylcylopropyl enol silanes (**7**, **8**, and **9**) were heated in base-washed, sealed ampoules for 0.5–3 hr at 360–450°. The crude rearrangement products were quenched with methanolic hydrochloric acid and the resulting ketones were identified by comparison of VPC retention times with those of authentic samples. Material balances of ca. 80–95% were obtained when the rearrangements were done in benzene solution containing some triethylamine; pyrolysis of neat samples gave similar product distribution with ca. 50% recovery of material. Table I summarizes the ketone products obtained in these rearrangements.

As shown in Table I, one methylvinylcyclopropyl enol silane **14** was examined. Ether **14** was prepared from the corresponding cyclopropyl ethyl ketone by kinetic enolate quenching (vide supra) to give a nonseparable mixture (67:33) of geometric isomers. Unambiguous structure assignment to the major and minor components was not possible owing to the similar chemical shifts for the vinyl hydrogen of each isomer.[8] The data presented in Table I correspond to ca. 30% conversion of **14** into rearrangement products, although essentially the same product composition was obtained for 50% conversion. Authentic samples of the four possible products, hexahydroindan-2-ones **15** and **16**, were prepared from the cis and trans ketones **10b** and **11b**. Kinetic alkylation of the cis ketone **10b** by sequential treatment with lithium diisopropylamide and then methyl iodide furnished a single monomethyl product in 80% yield. This material was assigned structure **15a** on the basis of alkylation from the less hindered, convex face of **10b**. Epimerization of **15a** with methanolic sodium methoxide gave an equilibrium mixture in which **15a** was the major product (ratio **15a**:**15b** = 4.4:1). The analogous kinetic alkylation of the trans isomer **11b** also gave a single monomethyl derivative in 70% yield. Tentative structure assignment of this kinetic product as **16b** was based on a consideration of the stereoelectronic requirements for alkylation. In order to maintain maximum orbital overlap during bond formation, alkylation will occur from the quasi-axial direction ($\beta$ face of **11b**) to yield the less stable isomer **16b**.[12] Confirmation of this assignment was obtained by base-catalyzed epimerization of the kinetic product **16b** to yield the more stable epimer **16a** (ratio **16a**:**16b** = 11:1). Appropriate control experiments showed that the epimers of ketones **15** and **16** did *not* equilibrate under the methanolic hydrochloric acid conditions used to hydrolyze the cyclopentene enol ether products.

An attempt to prepare the 8-methylhexahydroindanone **17** by this general sequence was thwarted at an early stage in that attempted distillation of ketone **18** resulted in formation of the exocyclic methylene derivative **19**. Formation

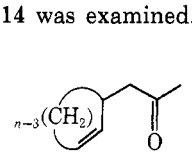


**17** **18** **19**

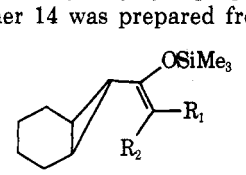
of **19** from **18** is readily explained by a thermal homo[1,5]hydrogen shift involving the cisoid carbonyl and methyl groups (an enolene rearrangement[13]).

## Discussion

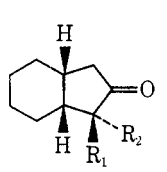
Examination of the data in Table I indicates that the formation of cyclopentanone products via the scheme outlined in eq 1 depends critically on the structure of the starting vinylcyclopropyl enol silane, **8** and **9**. Rearrangement of the angular-substituted enol derivatives **9b** and **9c** proceeds in good yield to give 1-hydroindanone (**12b**) and 1-hydroazulenone (**12c**). In contrast, the exo enol silane derivatives **8** yield two distinct types of products, the expected 3,4-disubstituted cyclopentanones **5** and monocyclic, $\gamma,\delta$-unsaturated ketones **13**. The formation of unsaturated ketones **13** is readily rationalized by postulating an initial isomerization[14] of the exo starting material **8** into the endo isomer **20**, followed by a facile homo[1,5]hydrogen shift[13] to



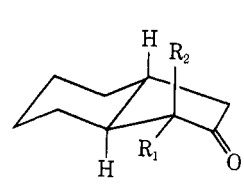
**13a**, $n = 5$
**b**, $n = 6$
**c**, $n = 7$



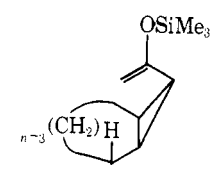
**14a**, $R_1$ = Me; $R_2$ = H
**b**, $R_1$ = H; $R_2$ = Me



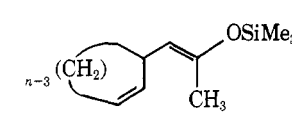
**15a**, $R_1$ = Me; $R_2$ = H
**b**, $R_1$ = H; $R_2$ = Me



**16a**, $R_1$ = Me; $R_2$ = H
**b**, $R_1$ = H; $R_2$ = Me



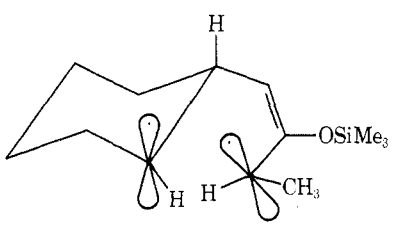
**20**



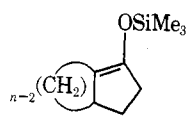
**21**

give ketone **13** after hydrolysis of the intermediate enol silane **21**. The major products observed from both the bicyclo[3.3.0]octan-3-one precursor **8a** and the hydroazulenone precursor **8c**, ketones **13a** and **13c**, respectively, result from this competing thermal process. In the case of the six-membered ring substrate **8b**, the major products were the annulated hydroindanones **10b** and **11b** together with a smaller amount of **13b**. In the bridgehead-substituted series **9** the analogous exo-endo isomerization would result in the highly strained trans-fused bicyclo[*n*.1.0]skeleton. Accordingly the vinylcyclopropane–cyclopentene rearrangement is the only thermal process observed in this series.

It is interesting to note that both the cis and trans hydroindanones **10b** and **11b** are formed in appreciable yield from **8b** and that the cis:trans ratio (~1:2) remains constant over the range of low to high conversion of starting material to products. Mechanistically the formation of **10b** and **11b** is consistent with either a diradical process[15] or a concerted pathway[16] ($_{\pi}2_a$, $_{\sigma}2_s \rightarrow$ **10**; $_{\pi}2_s$, $_{\sigma}2_a \rightarrow$ **11**). A potential way to distinguish between these possibilities would be to examine the rearrangement of the unhindered, maximally labeled[16] trans vinylcyclopropyl enol silane **14a**. At least three distinct pathways need to be considered for the rearrangement of **14a**: the orbital symmetry allowed process which would yield the cis ketone **15a** ($_{\pi}2_a$, $_{\sigma}2_s$) and the trans ketone **16a** ($_{\pi}2_s$, $_{\sigma}2_a$); a completely random stepwise (diradical) process which would give a mixture of the four possible hexahydroindanones **15** and **16**; and a diradical process involving an intermediate analogous to **22** in which




**22**




**23**, $n = 5, 6,$ or 7

the conformationally restricted[17] allyl radical adopts an equatorial position on the cyclohexane ring. If closure of **22** to a five-membered ring occurs before geometric isomerization of the allylic radical, a consideration of molecular models suggests that the preferred modes of closure of **22** would lead stereoselectively to ketones **15a** and **16a**, i.e., the products expected for the concerted reaction. Experimentally the rearrangement was carried out on the cis–trans mixture **14**. Since the rearrangement of the trans isomer of a cis–trans mixture is known to occur with greater facility,[18] the product distribution shown in Table I corresponds to ca. 30% conversion of starting material to products and should reflect the thermal behavior of the trans isomer **14a**. In practice, the major product observed in the rearrangement of **14**, trans ketone **16a**, supports either the first or third mechanistic possibility. These data, however, do not provide a basis for making an unambiguous distinction between these two pathways for the rearrangement of unhindered transoid vinylcyclopropanes.[19] It should be noted that preferential ring closure of diradical **22** to give the trans-fused product **16a** might be expected based on analogy to cationic olefin ring closures.[20]

The reaction conditions necessary to rearrange the oxygen-substituted vinylcyclopropanes **1** to **2** are comparable to those for simple vinylcyclopropane substrates and considerably more severe than the conditions necessary to rearrange the heteroatom-substituted derivatives shown in eq 2[4a] and 3.[6] In both of the latter cases the heteroatom is located on a carbon atom directly involved in the bond-making, bond-breaking process, and it may provide assistance in the rearrangement. For substrates of structure **1**, the oxygen atom is located at an $sp^2$-hybridized carbon atom in both the reactant and the product and it will have only a minimal effect on the net transformation.

In summary, the cyclopentanone annelation sequence shown in eq 1 provides a reasonable synthetic route to 2,3-disubstituted cyclopentanones such as **12b** and **12c**. Furthermore, the initial rearrangement products derived from enol silanes of general structure **9**, the cyclopentene enol derivatives **23**, can serve as regioselective precursors[21] to the *more* substituted enolate anion of ketones **12**.

## Experimental Section

**General.** Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 237B grating infrared spectrometer in carbon tetrachloride solution unless otherwise stated. NMR spectra were measured on a Varian Associates A-60 or a Perkin-Elmer R-12 spectrometer in carbon tetrachloride solution and chemical shifts are reported in parts per million downfield ($\delta$) from internal $Me_4Si$. Gas chromatography analyses were performed on a Varian Aerograph 1200 using a 3% SE-30 on Varaport 30 column (10 ft × 1/16 in.). Combustion analyses were done by Chemalytics, Inc., Tempe, Ariz.

**Cyclopropyl Ketones.** Cyclopropyl methyl ketone[22] and 1-acetylbicyclo[4.1.0]heptane (**4b**)[11] were obtained as indicated.

**6-Acetylbicyclo[3.1.0]hexane (3a).** Using the general procedure of Jorgenson,[10] bicyclo[3.1.0]hexane-6-carboxylic acid[23] furnished a 92% yield of **3a**: bp 66–68° (7 mm) [lit.[24] bp 60–63° (10 mm)]; ir ($CCl_4$) 1700 $cm^{-1}$ (C=O); NMR ($CCl_4$) $\delta$ 2.10 (s, 3, $CH_3C$=O) and 0.9–2.0 ppm (m, 9).

**7-Acetylbicyclo[4.1.0]heptane (3b).** Using the general procedure of Jorgenson,[10] bicyclo[4.1.0]heptane-7-carboxylic acid[25] furnished a 98% yield of **3b**: bp 39–40° (0.25 mm) [lit.[24] bp 83–86° (10 mm)]; ir ($CCl_4$) 1695 $cm^{-1}$ (C=O); NMR ($CCl_4$) $\delta$ 2.10 (s, 3, $CH_3C$=O), and 1.0–2.0 ppm (m, 11).

**8-Acetylbicyclo[5.1.0]octane (3c).** Using the general procedure of Jorgenson,[10] bicyclo[5.1.0]octane-8-carboxylic acid[26] furnished a 90% yield of **3c**: bp 80–83° (2 mm); ir ($CCl_4$) 1695 $cm^{-1}$ (C=O); NMR ($CCl_4$) $\delta$ 2.10 (s, 3, $CH_3C$=O), and 0.8–2.3 ppm (m, 13).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.93; H, 10.56.

**Ethyl Bicyclo[4.1.0]heptan-7-yl Ketone.** Using the general procedure of Jorgenson,[10] bicyclo[4.1.0]heptane-7-carboxylic acid[25] was treated with ethyllithium to furnish a 60% yield of product: bp 121–123° (29 mm); ir ($CCl_4$) 1670 $cm^{-1}$ (C=O); NMR ($CCl_4$) $\delta$ 0.98 (t, 3, $CH_3$), 1.0–2.2 (m, 11) and 2.48 ppm (q, 2).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.23; H, 10.35.

**1-Methyl-7-acetylbicyclo[4.1.0]heptane (18).** Using the general procedure of Jorgenson,[10] 1-methylbicyclo[4.1.0]heptane-7-carboxylic acid[27] furnished a 100% yield of **18**: bp 50–54° (0.07 mm); ir ($CCl_4$) 1690 $cm^{-1}$ (C=O); NMR ($CCl_4$) $\delta$ 2.14 (s, 3, $CH_3C$=O), 1.1–2.1 (m, 9), and 1.10 ppm (s, 3, $CH_3$).

*Anal.* Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.12; H, 10.61.

Distillation of **18** at 1.3 mm, bp 90–95°, yielded two new products that showed carbonyl absorptions at 1715 $cm^{-1}$. The NMR spectrum of this mixture indicated the presence of both two vinyl hydrogens ($\delta$ 4.44 and 4.60 ppm) and a singlet vinyl methyl group ($\delta$ 1.43). Redistillation, bp 58–60° (2.0 mm), gave a single substance tentatively assigned as 1-(1-methylcyclohexen-2-yl)propan-2-one on the basis of spectral data: ir ($CCl_4$) 1715 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.0–2.3 (m, 10), 1.43 (s, 3), and 2.08 (s, 3). The initial rearrangement product is assigned structure **19** on the basis of the vinyl hydrogen absorptions.

**1-Acetylbicyclo[3.1.0]hexane (4a).** Using the general procedure of Corey,[11] acetylcyclopentene[28] furnished a 84% yield of **4a**: bp 95–96° (34 mm); ir ($CCl_4$) 1690 $cm^{-1}$ (C=O); NMR ($CCl_4$) $\delta$ 0.8 (m, 1, cyclopropyl H), 1.2–2.0 (m, 7), and 1.99 ppm (s, 3, $CH_3C$=O).

Anal. Calcd for $C_8H_{12}O$: C, 77.36; H, 9.76. Found: C, 77.31; H, 9.73.

**1-Acetylbicyclo[5.1.0]octane (4c).** Using the procedure of Corey,[11] acetylcycloheptene[29] furnished a 90% yield of **4c**: bp 49–53° (0.6 mm); ir ($CCl_4$) 1680 $cm^{-1}$ (C=O); NMR ($CCl_4$) $\delta$ 0.7 (m, 1, cyclopropyl H), 1.1–2.2 (m, 10), and 1.96 ppm (s, 3, $CH_3C$=O).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.77; H, 10.41.

**Preparation of Enol Silanes. Method A.** To a solution of chlorotrimethylsilane (0.045 mol) and triethylamine (0.07 mol) in dimethylformamide (20 ml) in a nitrogen atmosphere was added 0.03 mol of cyclopropyl alkyl ketone. The solution was heated under reflux for 20 hr, allowed to cool to room temperature, and then diluted with pentane (150 ml). The organic phase was separated, washed with cold 50% saturated sodium bicarbonate solution (150 ml), and dried ($MgSO_4$), the pentane was removed in vacuo, and the residue was distilled to give product enol silane.

**Method B.** A tetrahydrofuran solution of lithium diisopropylamide (0.015 mol) was prepared by adding diisopropylamine to *n*-butyllithium at −78°. The solution was stirred for 1 hr after the addition. The cyclopropyl alkyl ketone (0.013 mol) was then added dropwise by syringe to the amide solution and the resulting mixture was stirred for 3 hr. The resulting enolate was quenched with excess chlorotrimethylsilane (0.04 mol) and the mixture was stirred for 1 hr. The excess chloromethylsilane was removed in vacuo and the residue was extracted with pentane. The pentane was removed in vacuo and the residue was distilled to give product enol silane.

**1-Trimethylsiloxy-1-cyclopropylethylene (7)** was prepared by method A to give 65% of enol silane **7**: bp 74–76° (71 mm); ir ($CCl_4$) 1650 $cm^{-1}$ (C=C); NMR ($CCl_4$) $\delta$ 0.17 (s, 9, $SiCH_3$), 0.50 (m, 5, cyclopropyl H), 3.76 (d, 1, $J$ = 1 Hz), 4.07 (d, 1, $J$ = 1 Hz).

Anal. Calcd for $C_8H_{16}OSi$: C, 61.48; H, 10.24. Found: C, 61.36; H, 10.38.

**1-Trimethylsiloxy-1-(bicyclo[3.1.0]hexan-6-yl)ethylene (8a)** was prepared by method A to give a 72% yield of enol silane **8a**: bp 82–83° (8 mm); ir 1650 $cm^{-1}$ (C=C); NMR ($CCl_4$) $\delta$ 0.10 (s, 9, $SiCH_3$), 0.8–2.0 (m, 9), 3.78 (broad s, 1), and 3.86 ppm (broad s, 1).

Anal. Calcd for $C_{11}H_{20}OSi$: C, 67.28; H, 10.27. Found: C, 67.07; H, 10.22.

**1-Trimethylsiloxy-1-(bicyclo[4.1.0]heptan-7-yl)ethylene (8b)** was prepared by method A to give a 67% yield of enol silane **8b**: bp 42–43° (0.1 mm); ir ($CCl_4$) 1645 $cm^{-1}$ (C=C); NMR ($CCl_4$) $\delta$ 0.15 (s, 9, $SiCH_3$), 0.9–2.0 (m, 11), 3.84 (d, 1, $J$ = 1 Hz), and 3.92 ppm (d, 1, $J$ = 1 Hz).

Anal. Calcd for $C_{12}H_{22}OSi$: C, 68.48; H, 10.55. Found: C, 68.78; H, 10.84.

**1-Trimethylsiloxy-1-(bicyclo[5.1.0]octan-8-yl)ethylene (8c)** was prepared by method B to give a 91% yield of enol silane **8c**: bp 84–94° (0.8 mm); ir ($CCl_4$) 1640 $cm^{-1}$ (C=C); NMR ($CCl_4$) $\delta$ 0.15 (s, 9, $SiCH_3$), 0.7–2.3 (m, 13), 3.81 (broad s, 1), and 3.92 ppm (broad s, 1).

Anal. Calcd for $C_{13}H_{24}OSi$: C, 69.57; H, 10.77. Found: C, 69.56; H, 11.07.

**1-Trimethylsiloxy-1-(bicyclo[3.1.0]hexan-1-yl)ethylene (9a)** was prepared by method B to give a 78% yield of enol silane **9a**: bp 42–44° (0.7 mm); ir ($CCl_4$) 1650 $cm^{-1}$ (C=C); NMR ($CCl_4$) $\delta$ 0.17 (s, 9, $SiCH_3$), 0.45 (m, 1, cyclopropyl H), 1.4–2.0 (m, 7), 3.9 (broad s, 1), and 4.02 ppm (broad s, 1).

Anal. Calcd for $C_{11}H_{20}OSi$: C, 67.28; H, 10.26. Found: C, 66.96; H, 10.47.

**1-Trimethylsiloxy-1-(bicyclo[4.1.0]heptan-1-yl)ethylene (9b)** was prepared by method B to give 80% yield of enol silane **9b**: bp 75–85° (0.1 mm); ir ($CCl_4$) 1640 $cm^{-1}$ (C=C); NMR ($CCl_4$) $\delta$ 0.18 (s, 9, $SiCH_3$), 0.6 (m, 1, cyclopropyl H), 0.7–2.4 (m, 10), 3.9 (broad s, 1), and 4.3 ppm (broad s, 1).

Anal. Calcd for $C_{12}H_{22}OSi$: C, 68.51; H, 10.47. Found: C, 68.50; H, 10.36.

**1-Trimethylsiloxy-1-(bicyclo[5.1.0]octan-1-yl)ethylene (9c)** was prepared by method B to give a 80% yield of enol silane **9c**: bp 55–60° (0.3 mm); ir ($CCl_4$) 1620 $cm^{-1}$ (C=C); NMR ($CCl_4$) $\delta$ 0.17 (s, 9, $SiCH_3$), 0.9–2.6 (m, 10), 4.0 (broad s, 1).

Anal. Calcd for $C_{13}H_{24}OSi$: C, 69.57; H, 10.77. Found: C, 69.31; H, 11.07.

**1-Trimethylsiloxy-1-(bicyclo[4.1.0]heptan-7-yl)propylene (14)** was prepared by method A to give a 90% yield of enol silanes **14**: bp 99–106° (6 mm); ir ($CCl_4$) 1668 $cm^{-1}$ (C=C); NMR (neat) $\delta$ 0.10 (s, 3, $SiCH_3$), 0.18 (s, 6, $SiCH_3$), 0.7–2.5 (m, 11), 1.43 (d, 2.1, $J$ = 7 Hz), 1.61 (d, 0.9, $J$ = 7 Hz), 4.44 (q, 0.7, $J$ = 7 Hz), and 4.50 ppm (q, 0.3, $J$ = 7 Hz). VPC analysis (3% SE-30, 130°) indicated a 67:33 mixture.

Anal. Calcd for $C_{13}H_{24}OSi$: C, 69.58; H, 10.78. Found: C, 69.98; H, 10.42.

**Pyrolysis of Trimethylsilyl Enol Silanes. Method A.** The appropriate enol silane (45 mg) in benzene (50 $\mu$l) was placed in a base-washed ampoule and then degassed and sealed under high vacuum. The tubes were heated in a furnace at 360° (2 or 3 hr) or at 400° (0.5 or 1 hr) depending on the sample. After cooling the tubes were opened and a solution of 0.04 *N* HCl (50 $\mu$l) in methanol was added to the pyrolysis products. This mixture was allowed to stand for 2 hr. An internal standard, cyclohexanone (25 $\mu$l), was added and mixture was analyzed on a Varian Aerograph Model 1200 gas chromatograph using 3% SE-30 (10 ft × 1/16 in.) at 100 and 125°, by comparison of retention times of products with known samples.

**Method B.** The appropriate enol silane (45 or 250 mg), an internal standard, decane (10 or 100 $\mu$l), and triethylamine (10 or 100 $\mu$l) in benzene (50 or 150 $\mu$l) were placed in a base-washed ampoule and then degassed and sealed under high vacuum. Pyrolyses were carried out as indicated in method A. The cooled samples were treated with 4 ml of 0.04 *N* HCl in THF for 10 min. Water (10 ml) and pentane (10 ml) were added and the organic phase was analyzed as described above.

The enol silanes examined by method A were **7**, **8a**, **8b**, **9a**, and **14** and those by method B were **8c**, **9b**, and **9c**. The products obtained are given in Table I and these results represent data from three or more individual runs. In general the final reaction mixtures contained ca. 70% products and 30% recovered cyclopropyl ketone. Material balances of 80–95% were obtained for method B; for method A material balances were 50–70%.

**Rearrangement products** were prepared as indicated: **10a**,[30] **10b**,[31] **10c**,[32] **11a**,[30] **11b**,[31] **12a**,[33] **12c**,[34] **and 13a**.[22]

***cis*-Hexahydroindan-1-one (12b).** A solution of 1-indanone (5.1 g, 0.04 mol) in ethanol (200 ml) containing 5% Rh/C (0.5 g) was hydrogenated at room temperature for 24 hr at 1750 psi. After filtering the solvent was evaporated in vacuo and the residue was distilled to give 2.8 g (52%) of 1-hexahydroindanol, bp 52–55° (0.04 mm). This alcohol was oxidized by the method of Brown[35] to give a 90% yield of **12b**, bp 41–44° (0.5 mm) [lit.[36] bp 82–87° (10 mm)].

**1-(Cyclohexen-3-yl)propan-2-one (13b)** was prepared from 3-bromocyclohexene[37] and ethyl acetoacetate by the method of Van Tamelen[38] to give a 33% yield of **13b**: bp 98–103° (26 mm); semicarbazone mp 171–173° (lit.[39] mp 170–171°); ir ($CCl_4$) 1720 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.9–2.1 (m, 7), 2.05 (s, 3), 2.42 (m, 2), and 5.54 ppm (m, 2).

**1-(Cyclohepten-3-yl)propan-2-one (13c)** was prepared as described for **13b** to give a 30% yield of **13c**: bp 90–95° (18 mm); ir ($CCl_4$) 1715 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.95–2.0 (m, 9), 2.00 (s, 3), 2.40 (m, 2), and 5.50 ppm (m, 2).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.84; H, 10.74.

***syn*-1-Methyl-*cis*-hydroindan-2-one (15a).** *cis*-Hydroindan-2-one (**10b**, 0.93 g, 6.8 mmol) was added dropwise at 0° to a THF solution (5 ml) of lithium diisopropylamide, prepared from methyllithium (8.8 mmol) and diisopropylamine (1.0 g, 10 mmol). After stirring for 1 hr at 0°, excess methyl iodide (6.9 g, 48 mmol) was added and the mixture was allowed to warm to room temperature. Water was added and the mixture was extracted with ether. The organic phase was dried ($MgSO_4$) and evaporated in vacuo and the residue was distilled to give 0.88 g (88%) of **15a**: bp 55–57° (0.6 mm); ir ($CCl_4$) 1747 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.99 (d, 3, $J$ = 7 Hz) and 0.9–2.7 ppm (m, 13).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.77, H, 10.62.

**Epimerization of 15a.** A sample of **15a** (19 mg) was allowed to stand in methanol (4 ml) containing a trace of sodium methoxide. After 4 hr the NMR spectrum showed two methyl group doublets at $\delta$ 0.99 (**15a**) and 0.94 (**15b**); VPC analysis indicated a ratio of **15a**: **15b** of 4.4:1. This ratio was the same after 20 hr.

***anti*-1-Methyl-*trans*-hydroindan-2-one (16b).** Using the procedure described above for **15a**, *trans*-hydroindan-2-one (**11b**, 0.86 g, 6.2 mmol) gave in 95% yield a mixture of recovered **11b** (15%), monoalkylated product **16b** (80%), and 5% of an unidentified substance. Pure **16b** was obtained by preparative VPC: ir ($CCl_4$) 1740 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.92 (d, 3, $J$ = 7 Hz) and 0.8–2.5 ppm (m, 13).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.82; H, 10.65.

**Epimerization of 16b.** A sample of **16b** (20 mg) was treated as described above for **15a**. After 1 hr the NMR spectrum showed two methyl doublets at $\delta$ 0.92 (**16b**) and 1.00 ppm (**16a**); after 20 hr VPC analysis indicated a ratio of **16a**:**16b** of 11:1.

**Control Experiments.** Treatment of either **15a** or **16b** with methanol-*O*-*d* containing HCl gas for 16 hr did not result in any detectable incorporation of deuterium as judged by NMR (doublet methyl signals remained unchanged).

**Registry No.**—**3a,** 10330-37-7; **3b,** 10330-36-6; **3c,** 53927-14-3; **4a,** 29773-67-9; **4b,** 2862-90-0; **4c,** 53927-15-4; **7,** 42161-96-6; **8a,** 53927-16-5; **8b,** 53927-17-6; **8c,** 53927-18-7; **9a,** 53927-19-8; **9b,** 53927-20-1; **9c,** 53927-21-2; **10b,** 5689-04-3; **11b,** 16484-17-6; **12b,** 2826-65-5; **13b,** 18955-93-6; **13b** semicarbazone, 53927-22-3; **14a,** 53927-23-4; **14b,** 53927-24-5; **15a,** 28436-04-6; **15b,** 28436-03-5; **16a,** 53927-25-6; **16b,** 53927-26-7; **18,** 53927-27-8; **19,** 53927-28-9; cyclopropyl methyl ketone, 765-43-5; ethyl bicyclo[4.1.0]heptan-7-yl ketone, 53927-29-0; 1-(1-methylcylclohexen-2-yl)propan-2-one, 53927-30-3; chlorotrimethylsilane, 75-77-4; 1-indanone, 83-33-0; 1-hexahydroindanol, 53927-31-4.

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# A Study of the Enamino Ketone Variant of the Robinson Annelation


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The mechanism of the enamino ketone variant of the Robinson annelation has been clarified. Isomeric enamino ketones **10** and **11** were prepared by methylation of the cross- and fully conjugated enolate anions of cyclic enamino ketone **5,** and both isomers gave the same mixture of dimethyl-3,4,8,8a-tetrahydro-1,6(2*H*,7*H*)-naphthalenediones on reaction with methyl vinyl ketone. The annelation products are derived from a common trione intermediate, **13.** Efforts to alter the mechanistic course of the annelation reaction were unfruitful.


An important class of synthetic intermediates related to the Wieland–Miescher ketone[1] (**4,** R = H) can be prepared by Robinson annelations of 2-methylcyclohexane-1,3-dione with unsaturated ketones like **2.** In the procedure described by Newman and Ramachandran[2] a base-catalyzed Michael reaction generates the triketone **3,** which then undergoes aldol cyclization on treatment with pyrrolidine in benzene. A variant of this approach, developed by Coates and Shaw,[3] uses the monopyrrolidine enamine **5** derived from the 1,3-diketone reactant and employs a heterogeneous reaction medium incorporating a buffered acetic acid catalyst (Scheme I).

Coates and Shaw found that reaction of 3-penten-2-one (**2,** R = $CH_3$) with **5** gave predominantly the trans diketone **4** (R = $CH_3$) accompanied by small amounts of the cis isomer. However, by using a more polar solvent such as dimethylformamide or dimethyl sulfoxide, they were able to obtain higher proportions of the cis isomer (e.g., 1:1).

Two distinct mechanisms for this modified annelation procedure can be conceived (Scheme II).

An initial acid-catalyzed Michael addition should generate an intermediate (**6**), which could then be hydrolyzed to **3** followed by pyrrolidine-induced aldol cyclization (mechanism A). Other mechanisms leading to intermediate **3** can also be envisaged (e.g., hydrolysis of **5** to **1** followed by conventional annelation, as in mechanism A′), but for the purposes of this discussion they need not be distinguished from mechanism A. Alternatively, the immonium intermediate **6** could undergo aldol-like cyclization to a nitrogen-containing precursor (**7**) of diketone **4** (mechanism B), as