Isomerization of *exo*-3 and *endo*-3.[15]—A 50-mg sample of fraction 3 from above was heated to 110° in trifluoroacetic acid for 60 hr under nitrogen, diluted with water, neutralized with solid $NaHCO_3$, extracted with ether, dried (Na_2SO_4), and concentrated. Nmr analysis showed a 33:67 mixture of *exo*-3 and *endo*-3 respectively.

Registry No.—1, 497-38-1; *exo*-**2**, 41828-85-7; *endo*-**2**, 41828-86-8; *endo*-**3**, 41828-87-9; *endo*-**3** semicarbazone, 41828-88-0; *exo*-**3**, 41828-89-1; *N*-ethyl-*N*-nitrosourethane, 614-95-9; bicyclo[3.2.1]octan-2-one, 5019-82-9; methyl iodide, 74-88-4; bicyclo[3.2.1]octan-3-one, 5019-82-9.

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[15] Attempted isomerization with sodium methoxide in methanol led to a complex reaction mixture, apparently owing to aldol condensations.

Preparation of 4-Phenyl Medium- and Large-Sized Ring Ketones

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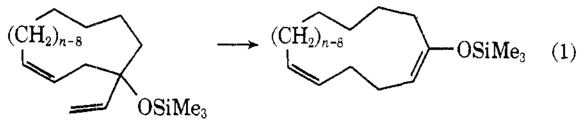
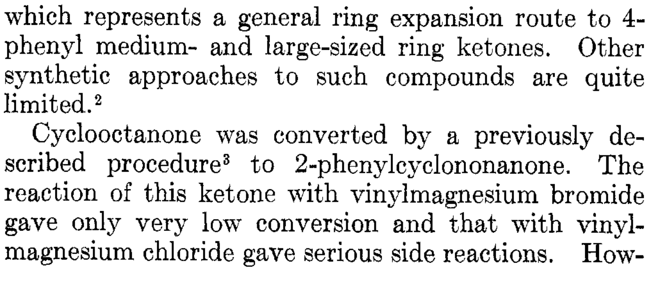
Received May 21, 1973

Previous studies in these laboratories[1] have described the siloxy-Cope rearrangement as a ring expansion for medium-sized rings (*e.g.*, eq 1). The present work shows that 2-phenyl-1-trimethylsiloxy-1-vinylcyclononane (1) undergoes a related rearrangement which represents a general ring expansion route to 4-phenyl medium- and large-sized ring ketones. Other synthetic approaches to such compounds are quite limited.[2]



(1)

$n = 8, 9, 10$



Cyclooctanone was converted by a previously described procedure[3] to 2-phenylcyclononanone. The reaction of this ketone with vinylmagnesium bromide gave only very low conversion and that with vinylmagnesium chloride gave serious side reactions. However, the reaction with vinyllithium gave a 60% conversion to the vinyl alcohol. The incomplete reaction presumably arises because enolate anion formation competes with the desired reaction. The conversion can be increased by allowing the crude mixture to react again (*ca.* 75% conversion). Alternatively, the unreacted ketone can be readily removed by chromatography and recycled. Trimethylsilylation of the alcohol gives complete conversion to **1**.

Heating **1** in sealed ampoules in the 210–280° temperature range gave enol ethers corresponding to a [1,3] sigmatropic shift and also the corresponding ketone **2**. Hydrolysis of the mixture gave **2** in 80% overall yield from **1**.

The structure of **2** was assigned from the nmr spectrum and from decoupling experiments carried out on samples in which the chemical shifts had been separated with $Eu(fod)_3$. Thus sufficient shift reagent was added so that the α-proton multiplet moved to δ 5.0, the benzylic proton (a broad triplet) to δ 4.5, and three of the β protons to δ 3.9.[4] Decoupling established that the benzylic proton was coupled to the β protons, which were in turn coupled to the α protons, thus establishing the position of the phenyl on the ring.

Kinetic measurements were made (Table I); however, the data were somewhat erratic and gave activation parameters that are unreasonable for a simple process ($E_a = 25.4$ and $\log A = 5.5$). Presumably a major part of the reaction involves some sort of surface catalysis or radical chain process. This process apparently causes formation of ketone during the pyrolysis, which is not normal for this type of reaction. Major amounts of ketone were formed with this system even when the ampoules were carefully dried.

Table I

Ampoule Pyrolysis of 2-Phenyl-1-trimethylsiloxy-1-vinylcyclononane (1)

Temp, °C	Time, hr	% 2[a,b]	% nonvolatile[b]
213	11.75	42	
	24	58	
225	6	44	
	12	63	
260	6	30	
	12	66	
	18	74	
280	6	59	12
	12	74	17
310	0.67	58	41
330	0.67	52	48

[a] Measured after hydrolysis of the pyrolysis mixture. [b] Yield and nonvolatile were determined by gc using an internal standard.

Although the reaction is not kinetically well behaved, it is high yield and clean in the sense that it leads to a single product after hydrolysis. The success of the reaction depends on the balance between the change in ring strain and the favorable energy change associated with formation of the enol (*ca.* 4.5 kcal/mol[5]). By analogy with the related systems shown in eq 1, the reaction should be feasible for rings larger than eight membered.

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[1] (a) R. W. Thies, *Chem. Commun.*, 237 (1971); (b) R. W. Thies, *J. Amer. Chem. Soc.*, **94**, 7074 (1972); (c) R. W. Thies, M. T. Wills, A. W. Chin, L. E. Schick, and E. S. Walton, *ibid.*, **59**, 5281 (1973); (d) R. W. Thies and J. E. Billigmeier, 161st National Meeting of the American Chemical Society, Los Angeles, Calif, March 28–April 12, 1971, Abstract 162.

[2] For syntheses of 4-phenylcyclooctanone see A. C. Cope and R. B. Kinnel, *J. Amer. Chem. Soc.*, **88**, 752 (1966); A. C. Cope and R. B. Kinnel, *ibid.*, **89**, 5995 (1967); A. C. Cope, M. A. McKervey, and N. M. Weinshenker, *ibid.*, **89**, 2932 (1967).

[3] A. J. Sisti, *J. Org. Chem.*, **33**, 453 (1968). For an alternative method, see E. Müller and R. Heischkeil, *Tetrahedron Lett.*, 1032 (1962).

[4] The remainder of the spectra consists of the phenyl protons at δ 7.2 and 7.6, a two-proton multiplet containing the remaining β proton at δ 3.2, and a large multiplet at δ 2.9–1.8.

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

Experimental Section

General.—Spectra were recorded on Beckman IR-8, Varian HA-100, Atlas CH7, and CEC 110B instruments.[6] Varian-Aerograph 1200 and A90P instruments were used for glc with columns (A) 0.01 in. × 25 ft UCONLB550X capillary, (B) 0.125 in. × 7 ft 2.5% KOH–2.5% Carbowax 4000 on 80/100 Chromosorb W, and (C) 0.25 in. × 4 ft 20% SF96 on Chromosorb. Analyses were performed at Galbraith Laboratories.

2-Phenyl-1-trimethylsiloxy-1-vinylcyclononane (1).—A solution of 1 g (4.7 mmol) of 2-phenyl-1-cyclononanone[8] in 5 ml of dry THF was added under nitrogen at room temperature to 15 ml of 1 *M* vinyllithium in THF (diluted Ventron solution). The reaction was stirred for 15 min and was then quenched with 5 ml of saturated ammonium chloride and extracted with pentane. The pentane solution was washed with water and dried over magnesium sulfate. Analysis by gc (column A at 135°) showed a 60% conversion (other runs with longer reaction times did not give significantly greater conversion). The alcohol was purified by chromatography on SilicAR, eluting with pentane to remove a substantial amount of nonpolar material and then with 3% ether–pentane, which gave unreacted ketone (36%) and the desired alcohol[7] (45% yield) as a low-melting solid: ir (CS_2) 2.8, 3.42, 14.4 μ; nmr (CCl_4) δ 7.12 (s, 5), 5.82, 4.74, 4.68 (ABC pattern, J = 12, 17 Hz, 3), 2.8 (m, 1), 1.0–1.8 (m, 15).

The alcohol was converted to the trimethylsilyl derivative by stirring with Tri-Sil Concentrate (Pierce Chemical Co.) and dimethyl sulfoxide as described previously.[1b] The product was purified by preparative gas chromatography on column C at 160°, which gave 1 as a semisolid: ir (neat) 3.42, 6.75, 6.90, 8.04, 9.42, 11.15, 12.0, 13.3, 14.35 μ; nmr (CCl_4) δ 7.2 (m, 5), 5.52, 4.92, 4.84 (ABC pattern, J = 17, 10, 2 Hz, 3), 2.8 (m, 1), 1.2–2.2 (m, 14), 0.12 (s, 9); mass spectrum m/e 316.221 (calcd for $C_{20}H_{32}OSi$, m/e 316.222).

4-Phenylcycloundecanone (2).—Ampoules were prepared and sealed as described previously.[1b] The ampoules were heated in an aluminum block oven which was regulated with a Cole Palmer Model 1300 temperature controller. Most runs utilized 10 mg of gc-purified sample in a 10-ml ampoule. A run using a 0.8-ml ampoule and 0.2 g of sample that had only been purified by vacuum transfer gave similar results when heated for 16 hr at 280° except that the amount of ketone formed during pyrolysis was much higher (64% *vs.* 13%) and the yield was only 60%. Analysis of the product mixture before hydrolysis using a glc–mass spectrometer combination (column B) showed two rearranged trimethylsilyl compounds and a third component which was identified as 2.

Hydrolysis of the mixture as described earlier[1b] gave only one product, 2: ir (neat) 3.42, 5.88, 6.70, 6.90, 13.25, 14.35 μ; nmr (CCl_4) δ 7.5 (m, 5), 2.4–2.9 (m, 5), 1.3–2.1 (m, 14).

Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.89. Found: C, 83.23; H, 9.67.

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

Registry No.—1, 42031-17-4; 2, 42031-18-5; 2-phenyl-1-cyclonanone, 14996-80-6.

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[6] We thank the University of Oregon for the use of their CEC mass spectrometer.

[7] Two diastereomers are possible. The alcohol used showed only one peak on gc (columns A and B). The later chromatography fractions (not used) showed minor amounts of another alcohol with a slightly longer retention time.

Di- and Trimethyl-2-cyclohexenones

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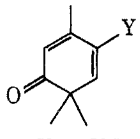
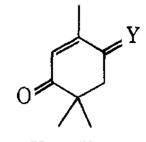
In connection with a problem of terpene synthesis 4-methoxy-3,6,6-trimethyl-2,4-cyclohexadienone (**1a**) was needed as starting material as a consequence of which the following reactions were investigated.

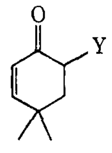


1a, Y = OMe
b, Y = H

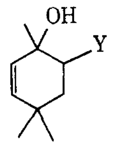


2a, Y = H_2
b, Y = H, Br
c, Y = H, OAc
d, Y = O
e, Y = H, OMe

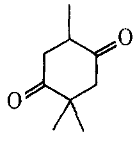
Treatment of 3,6,6-trimethyl-2-cyclohexenone (**2a**),[1] prepared by the interaction of methylmagnesium iodide with 4,4-dimethyl-2-cyclohexenone (**3a**)[2] followed by chromic acid oxidation of the resultant carbinol (**4a**), with *N*-bromosuccinimide yielded bromo ketone **2b**, which suffered facile dehydrobromination producing dienone **1b** but could be converted into the keto ester **2c** on exposure to silver acetate. Lithium aluminum hydride reduction of **2c**, followed by manganese dioxide oxidation of the intermediate diol, gave the diketone **2d**. Unfortunately, neither ketalation of the latter or its dihydro derivative **5** under a variety of conditions[3] nor enol ether formation of **2d** succeeded.



3a, Y = H
b, Y = Br
c, Y = OMe
d, Y = OAc
e, Y = OH



4a, Y = H
b, Y = OMe



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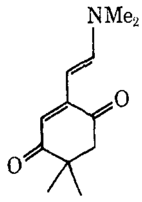

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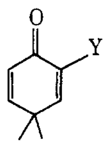
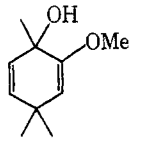
An alternative route toward the desired product was based on an attempt to introduce the methoxyalkene function into the framework of cyclohexenone **3a**. While selenium dioxide oxidation of the latter yielded dienone **7a**,[4] treatment of **3a** with cupric bromide afforded **3b**,[4] whose exposure to methanolic silver nitrate led to the keto ether **3c**. Interaction of the latter with methylmagnesium iodide and the resultant carbinol **4b** with chromic acid produced the ether **2e**. Unfortunately, various attempts to dehydrogenate **2e** failed.



7a, Y = H
b, Y = OH
c, Y = OMe



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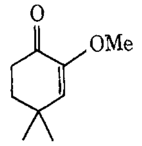

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[1] J. M. Conia and F. Rouessac, *Bull. Soc. Chim. Fr.*, 1925 (1963).

[2] (a) E. L. Eliel and C. A. Lukach, *J. Amer. Chem. Soc.*, **79**, 5986 (1957); (b) E. D. Bergmann and R. Corett, *J. Org. Chem.*, **23**, 1507 (1958); (c) J. M. Conia and A. Le Craz, *Bull. Soc. Chim. Fr.*, 1937 (1960); (d) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **28**, 1347 (1963); (e) J. W. Lewis and R. L. Meyers, *J. Chem. Soc. C*, 753 (1971).

[3] Treatment of **2d** with bis(dimethylamino)methoxymethane afforded the condensation product **6** [*cf.* R. F. Borch, C. V. Grudzinskas, D. A. Peterson, and L. D. Weber, *J. Org. Chem.*, **37**, 1141 (1972)].

[4] F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **28**, 2544 (1963).