Thermal Transformations of Medium-Ring Olefins

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Received August 26, 1970

The pyrolysis of cycloheptene, cyclooctene, cyclononene, and cyclododecene has been studied in a flow system at relatively high temperatures. Two major reaction processes obtain, namely isomerization of the cycloalkene to an α,ω-diene and to a ring-contracted vinylcycloalkane. Both of these reactions are reversible. Related transformations occur with 3- and 4-cyclooctenone. The details of these reactions are discussed.

In connection with photochemical studies on medium-ring ketones possessing nonconjugated double bonds,[2,3] it was of interest to compare the thermally induced transformations of such substrates. Two examples are described at the end of the present paper. In order to provide perspective for this work, a product survey on the pyrolysis of simple medium-ring olefins was performed.

Pyrolysis of either *cis*-cyclononene or *trans*-cyclononene at 720° in a flow system at reduced pressure promoted complete conversion to 1,8-nonadiene and vinylcycloheptane in a 4:1 ratio. The reaction was remarkably clean in that no other important products were observed. Resubmission of 1,8-nonadiene to the reaction conditions resulted in 65% conversion to 1,5-hexadiene and, significantly, a trace of both *cis*-cyclononene and vinylcycloheptane. The vinyl compound, on the other hand, was not substantially decomposed under the thermolysis conditions, although it gave detectable amounts of *cis*-cyclononene and 1,8-nonadiene. No *trans*-cyclononene was observed from the pyrolysis of either product. Thermolysis of *cis*- and *trans*-cyclononene at various temperatures led to variations in the product mixtures as summarized in Table I.

TABLE I

PYROLYSIS OF CYCLONONENE AT VARIOUS TEMPERATURES

Temp, °C	1	2	3	4	Ratio of 3/4
720	0[a]	0	80	20	4
620	54[a]	0	43	3	14
520	93[a]	0	67	0.3	23
720	0	0[a]	80	20	4
620	0	1[a]	92	7	13
520	0	49[a]	49	2	24

[a] Starting material.

Rearrangement of either *cis*-cyclododecene or *trans*-cyclododecene at 720° yielded 1,8-nonadiene, 1,11-dodecadiene, vinylcyclodecane, *cis*-cyclododecene, and *trans*-cyclododecene in the same 5:34:3:20:32 ratio. Resubmission of vinylcyclodecane to the reaction conditions produced 1,8-nonadiene, 1,11-dodecadiene, *cis*-cyclododecene, and *trans*-cyclododecene in a 5:34:20:32 ratio. 1,11-Dodecadiene, on the other hand, was 35% converted to 1,8-nonadiene as the sole product.

Pyrolysis of *cis*-cyclooctene produced 1,5-hexadiene, 1,7-octadiene, and vinylcyclohexane in a 3:78:14 ratio plus about 5% of uncharacterized lower molecular weight products. The vinyl compound was not substantially transformed to other materials under the reaction conditions, but careful gc analysis indicated a trace of cyclooctene and 1,7-octadiene. Thermolysis of 1,7-octadiene resulted in 35% conversion to 1,5-hexadiene and minute amounts of cyclooctene and vinylcyclohexane.

Pyrolysis of cycloheptene at 800° generated a complex product mixture. Six components in a 55:14:3:6:15:5 ratio were isolated in addition to 25% unreacted starting material and identified as vinylcyclopentane, 1,6-heptadiene, 4-methylcyclohexene, cyclopentadiene, benzene, and toluene. Submission of vinylcyclopentane or 1,6-heptadiene to the reaction conditions afforded essentially the same product mixture obtained from cycloheptene. At 800°, 4-methylcyclohexene was transformed completely to benzene and toluene in a 4:1 ratio and cyclopentene was converted to cyclopentadiene.

The isomerization of medium-ring olefins (**1** or **2**) to α,ω-dienes (**3**) was first reported by Blomquist[4] and later extended by Rienäcker.[5] The latter author also noted that pyrolysis of *cis*-cyclodecene under certain conditions gave about 5% of vinylcyclooctane in addition to 1,9-decadiene. The present work, which was performed at reduced pressure and generally higher temperatures, extends the range of observed transformation to α,ω-dienes and demonstrates the universal nature of the allylic rearrangement leading to ring-contracted vinylcycloalkanes (**4**). Considering the sum total of the data, it seems secure to conclude that both of these reactions are reversible. Reconversion of the α,ω-dienes to cycloalkenes is appreciable for the C_7 compound and small but clearly demonstrated reversion was observed for the C_8 and C_9 dienes. The reversibility of the C_8 system has been explored previously.[6] The C_{12} diene did not reclose but this is probably a result of its more facile fragmentation to give 1,9-nonadiene. The vinyl compounds showed trace reconversion to cycloalkenes for C_8 and C_9 systems and appreciable amounts with the C_7 and C_{12} compounds.

The identical nature of the product mixtures obtained from either geometrical isomer of cyclododecene or cyclononene (see Table I) is noteworthy and could indicate preequilibration ($\mathbf{1} \rightleftarrows \mathbf{2}$) or a common intermediate in these reactions. Geometrical isomerism is indeed observed for the C_{12} system. The trans C_8[6] and C_9 olefins are more reactive than their cis isomers as expected on the basis of the more strained nature of the smaller *trans*-cycloalkenes. The higher reactivity and lower thermodynamic stability of these trans olefins accounts for their nonaccumulation in the pyrolysates, but the

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(1) (a) Alfred P. Sloan Research Fellow, 1968–1970; (b) Petroleum Research Fund Graduate Fellow.

(2) J. K. Crandall, J. P. Arrington, and J. Hen, *J. Amer. Chem. Soc.*, **89**, 6208 (1967).

(3) J. K. Crandall, J. P. Arrington, and R. J. Watkins, *Chem. Commun.*, 1052 (1967).

(4) A. T. Blomquist and P. R. Taussig, *J. Amer. Chem. Soc.*, **79**, 3505 (1957); see also A. C. Cope and M. J. Youngquist, *ibid.*, **84**, 2411 (1962).

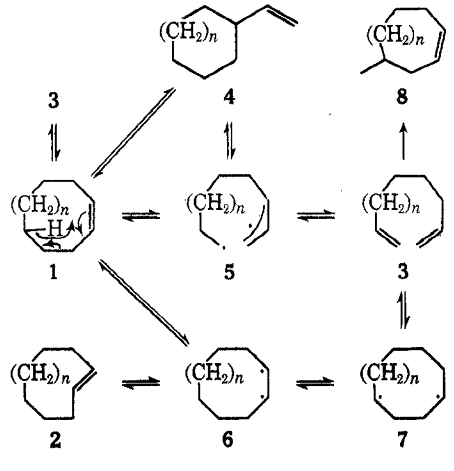
(5) R. Rienäcker, *Brennst.-Chem.*, **45**, 206 (1964).

(6) W. R. Roth, *Chimia*, **20**, 229 (1966).

lack of favorable trans to cis isomerization in the C_9 series speaks against cycloalkene preequilibration, unless only the trans isomer is reactive and it is transformed to products much more readily than it is isomerized to cis olefin. A more likely alternative is that the reaction pathway involves a common reactive intermediate which can be achieved from either cis or trans starting olefin.

The isomerization of cyclic olefins to α,ω-dienes is formally a reverse ene reaction.[7] This type of transformation is customarily considered to proceed by a concerted six-center mechanism, but stepwise, biradical conversions may obtain in certain instances. One such pathway involves homolysis of the allylic bond of the cycloalkene to give biradical **5** and disproportionation of this species (in just one of three possible ways) to yield α,ω-diene **3**. A second scheme proceeds by thermal activation of the olefin moiety to a vibrationally excited state best represented by biradical structure **6**; 1,5-hydrogen transfer (in one of two possible ways) then leads to 1,4-biradical **7** which can collapse to α,ω-diene in a straightforward fashion. Biradical **6**, of course, is the logical intermediate for cycloalkene geometrical isomerism[8] which was experimentally demonstrated for the C_{12} system. The reverse reaction (**3** → **1**) can be accommodated by any of the above mechanisms without insurmountable difficulty. It is interesting that the alternate ene reaction orientation (**3** → **8**) has been characterized only for the C_7 diene where 4-methylcyclohexene and its transformation products benzene and toluene are important components of the pyrolysis mixture. However, the minor extent of the cyclization reaction for the other α,ω-dienes may have obscured similar processes (see Scheme I).

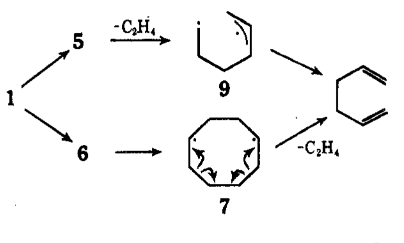
SCHEME I



The two more obvious mechanistic routes from cycloalkene to vinylcycloalkane **4** are concerted [1,3]-sigmatropic rearrangement[9] in which a methylene group migrates from one end of an allylic moiety to the other, or the nonconcerted equivalent proceeding through intermediate biradical **5**. Current dogma requires that the concerted process occurs with inversion of configuration at the migrating center.

If generalization from the data obtained for cyclononene (Table I) is valid, there is a strong temperature dependence on the **3**:**4** ratio, which decreases with increasing temperature in the C_9 system. This situation is best rationalized by competition between two processes with reasonably different activation parameters *at the product determining stage* of the reaction. Attractive possibilities include competition between (a) the two concerted reactions, (b) a concerted pathway to **3** and the biradical route to **4**, (c) two biradical pathways involving partitioning between alternate biradicals **5** and **6**, and (d) the two different decomposition modes of biradical **5**. A small bias in favor of the last alternative derives from the discussion above regarding the likelihood of a common intermediate from the *cis*- and *trans*-cycloalkene. However, clear distinction among the various possibilities must await more incisive experimentation, particularly the quantitative determination of activation parameters and further discussion is best deferred until this data is available.

In addition to the isomerization reactions induced by thermolysis of the cycloalkenes, various amounts of fragmentation to smaller hydrocarbons were observed. One relatively important such process involves conversion of the α,ω-diene to a lower α,ω-diene by the loss of a three-carbon fragment, propene. This reaction is a simple ene fragmentation and was characterized in the present study for the C_9 and C_{12} compounds. A less obvious fragmentation is the elimination of ethylene to give 1,5-hexadiene in the C_8 system. The formation of cyclopentadiene from cycloheptene is probably the result of a similar process involving the intermediacy of pentadienes[10] and cyclopentene.[11] It is interesting and perhaps significant that the loss of ethylene was not an important reaction with the higher homologs. One direct explanation for the loss of ethylene utilizes biradical **5** which can split out this small molecule with the formation of a new biradical **9**, a potential precursor of 1,5-hexadiene.[12] However, the operation of this mode of reaction of **9** to the exclusion of the other disproportionation and combination possibilities seems a little peculiar. Cyclohexene, which is not substantially decomposed by the pyrolysis conditions, is especially anticipated from **9**. An alternate and intriguing possibility invokes the indicated fragmentation of biradical **7**. A similar process can obtain for the C_7 system but not for the higher homologs, in accord with experimental observation.



With these results in hand, attention can be turned to the unsaturated carbonyl compounds alluded to above in connection with related photochemical studies. Pyrolysis of 4-cyclooctenone (**10**) at 720° gave 63% 3-

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[7] H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

[8] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, pp 72–75.

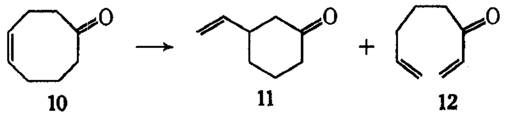
[9] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[10] For example, pyrolysis of piperylene under the indicated conditions gives partial conversion to cyclopentadiene.

[11] J. E. Baldwin, *Tetrahedron Lett.*, 2953 (1966); D. W. Vanas and W. D. Walters, *J. Amer. Chem. Soc.*, **70**, 4035 (1948).

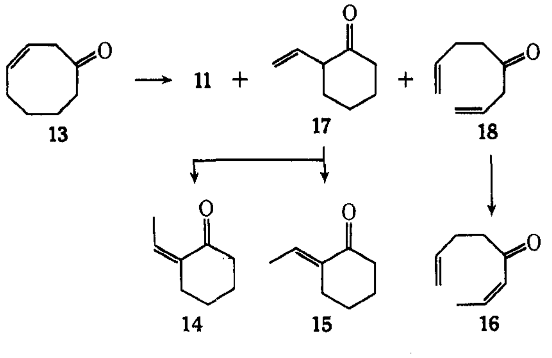
[12] Reference 8, pp 121–129.

vinylcyclohexanone (**11**), 10% octa-1,7-dien-3-one (**12**), and a host of uncharacterized minor components.[3] Thus the rearrangement of **10** parallels that of cyclooctene itself. The placement of the carbonyl function allows for only one mode for reverse ene reaction in this unsymmetrical system. The major product is the allylic rearrangement product **11** in which the migrating methylene group has an adjacent carbonyl function, presumably a beneficial situation. Little, if any of the other possible allylic isomerization product, 4-vinylcyclohexanone, is present. Interestingly, pyrolysis of 3-vinylcyclohexanone under these conditions was without effect.



10 **11** **12**

The thermolysis of 3-cyclooctenone (**13**) at 720° yielded *cis*- and *trans*-2-ethylidenecyclohexanone (**14** and **15**), 3-vinylcyclohexanone (**11**), and *cis*-octa-2,7-dien-4-one (**16**) in a 19:28:12:15 ratio. A plethora of minor products accompanied these important constituents. Compounds **14** and **15** are almost certainly secondary products derived from 2-vinylcyclohexanone (**17**), which is known to isomerize readily to these materials.[2] The acyclic ketone is probably also formed by secondary isomerization of octa-1,7-dien-4-one (**18**), the expected ene fragmentation product. In fact, careful examination of the spectral data indicates that there was about 20% **18** in the sample of **16**. Enolization and subsequent 1,5-hydrogen transfer accounts for the **18** → **16** transformation including the less stable cis stereochemistry of **16**. Insofar as the allylic isomerization is concerned, both possible processes appear to obtain. It is noteworthy that migration of the carbonyl carbon (**13** → **17**) is favored over that of the methylene group (**13** → **18**) though only by a factor of about 4.



13 **17** **18**

14 **15** **16**

Comparison of these results with the photochemical studies lead to the conclusion that, although there is some overlap of product from the two types of reactions, the thermal processes are much less specific and, furthermore, these appear to be regulated by the double bond and not by the carbonyl function as in the photochemical transformations.

Experimental Section

General.—Nmr spectra were obtained with a Varian HR-100 instrument (CCl$_4$) and infrared spectra (ir) with a Perkin-Elmer 137 spectrophotometer (neat samples). Gas chromatography (gc) was performed on Aerograph A1200 (analtyical) and A90-P3 (preparative) instruments. The analytical column was 10 ft × $^1/_8$ in. 15% Carbowax 20M on 60–80 Chromosorb W; the preparative column was 20 ft × $^1/_8$ in. 15% Carbowax 20M on 60–80 Chromosorb W. Percentage composition data on product mixtures were estimated by peak areas and are uncorrected. Mass spectra were obtained at 70 eV on an AEI-MS9 instrument. Starting materials were purified by preparative gas chromatography.

General Pyrolysis Procedure.—The thermal rearrangements were effected on a vacuum pyrolysis system consisting of a quartz column, 10 × 170 mm, packed with quartz chips passing through an E. H. Sargent and Co. tube furnace. The sample was placed in a 5-ml flask attached at one end of the tube and a trap, 20 × 150 mm, cooled with Dry Ice–acetone was attached to the other end of the tube. Vacuum was applied at the trap and the pyrolysate collected in the trap. Analysis of product mixtures was by analytical gc, while product separation was achieved by preparative gc.

***trans*-Cyclononene.**—A stirred solution of 6 g of *cis*-cyclononene[13] in 650 ml of benzene was irradiated for 7 hr using a 450 W Hanovia Type L mercury lamp without a filter. Removal of the solvent by distillation through a glass-helices packed column yielded 6 g of a mixture of *cis*-cyclononene and *trans*-cyclononene in a 4:1 ratio. The mixture was placed on a column containing 350 g of 20% silver nitrate–silica gel[14] and elution with pentane afforded, after evaporation of the solvent, 0.9 g (15%) of *trans*-cyclononene: ir 6.1 and 10.3 μ; nmr δ 5.3 (m, 2, CH=CH), 2.2 (m, 4, C=CCH$_2$), and 1.6 (m, 10, CH$_2$).

Pyrolysis of *cis*-Cyclononene.—Pyrolysis of 0.7 g of *cis*-cyclononene at 720° resulted in complete conversion to two products in a 4:1 ratio. The major product was identified as 1,8-nonadiene: ir 3.3, 6.07, 10.1, and 11.0 μ; nmr δ 5.7 (m, 2, C=CH), 4.9 (m, 4, C=CH$_2$), 2.05 (m, 4, C=CCH$_2$), and 1.35 (m, 6, CH$_2$). The minor product was identified as vinylcycloheptane:[15] ir 3.3, 6.1, 10.1, and 11.0 μ; nmr δ 5.7 (m, 1, C=CH), 4.8 (m, 2, C=CH$_2$), and a broad resonance from 2.2 to 1.2 accounting for thirteen ring protons; mass spectrum *m/e* (rel intensity) 124 (5), 109 (11), 96 (62), 95 (100), 81 (56), 67 (97), 55 (67), 54 (68), and 41 (69). No *trans*-cyclononene was observed.

Pyrolysis of *trans*-Cyclononene.—Pyrolysis of 0.3 g of *trans*-cyclononene at 720° resulted in complete conversion to 1,7-nonadiene and vinylcycloheptane in a 4:1 ratio. No *cis*-cyclononene was observed.

Pyrolysis of 1,8-Nonadiene.—Pyrolysis of 50 mg of 1,8-nonadiene at 720° resulted in 65% conversion to 1,5-hexadiene as well as a trace of *cis*-cyclononene and vinylcycloheptane.

Pyrolysis of Vinylcycloheptane.—A 25-mg sample of vinylcycloheptane was pyrolyzed under the reaction conditions and produced 1% *cis*-cyclononene and 1% 1,8-nonadiene.

***cis*-Cyclododecene and *trans*-Cyclododecene.**—A commercial sample of cyclododecene (Columbian Carbon Co.) was separated by preparative gc.

Pyrolysis of *cis*-Cyclododecene.—Pyrolysis of 1.1 g of *cis*-cyclododecene at 720° resulted in the formation of four products and starting material in the ratio 5:34:3:32:20. The products were separated by preparative gc from the 0.95 g (86%) of pyrolysate. The 5, 34, 32, and 20% products were identified as 1,8-nonadiene, 1,11-dodecadiene, *trans*-cyclododecene, and *cis*-cyclodododene, respectively, by comparison with authentic samples. The 3% product was identified as vinylcyclodecane: ir 3.3, 6.1, 10.05, and 11.0 μ; nmr δ 5.7 (m, 1, C=CH), 4.9 (m, 2, C=CH$_2$), a broad resonance from 2.3 to 2.1 (1, C=CCH), and a broad singlet at 1.55 (s, 18, CH$_2$); mass spectrum *m/e* (rel intensity) 166 (3), 137 (53), 109 (40), 95 (61), 81 (100), 67 (90), 55 (95), and 41 (94).

Pyrolysis of *trans*-Cyclododecene.—Pyrolysis of 0.5 g at 720° produced the same products in the same ratios as were observed from rearrangement of *cis*-cyclododecene.

Pyrolysis of 1,11-Dodecadiene.—Pyrolysis of a 10-mg sample of 1,11-dodecadiene under the reaction conditions resulted in 35% conversion to 1,8-nonadiene. No *cis*- or *trans*-cyclododecene was observed.

Pyrolysis of Vinylcyclodecane.—Pyrolysis of 5 mg of vinylcyclodecane at 720° produced 1,8-nonadiene, 1,11-dodecadiene, and *cis*- and *trans*-cyclododecene in a 5:34:32:20 ratio.

Pyrolysis of *cis*-Cyclooctene.—Pyrolysis of 1.5 g at 720° pro-

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(13) P. D. Gardner and M. Narayana, *J. Org. Chem.*, **26**, 3518 (1951).

(14) E. C. Murray and R. N. Keller, *ibid.*, **34**, 2234 (1969).

(15) Prepared by the method of G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Amer. Chem. Soc.*, **89**, 3652 (1967).

duced 1.3 g (86%) of pyrolysate. Gc analysis indicated 91% conversion to three products in a 78:14:3 ratio plus 5% of uncharacterized fragmentation products.

The major product was identified as 1,7-octadiene by comparison with an authentic sample. The 14% product was identified as vinylcyclohexane: ir 3.3, 6.1, 10.1, and 11.0 μ; nmr δ 5.7 (m, 1, $C=CH$), 4.85 (m, 2, $C=CH_2$), and broad multiplets at 1.7 and 1.2 accounting for eleven ring protons; mass spectrum *m/e* (rel intensity) 110 (29), 95 (18), 81 (100), 67 (68), 54 (36), and 41 (40). The minor product was 1,5-hexadiene.

Pyrolysis of Vinylcyclohexane.—A 0.3-g sample was pyrolyzed at 720° and found to be stable. Only 1% each of 1,7-octadiene and cyclooctene were produced.

Pyrolysis of 1,7-Octadiene.—Pyrolysis of 0.9 g under the reaction conditions resulted in 35% conversion to 1,5-hexadiene as well as a trace of cyclooctene and vinylcyclohexane.

Pyrolysis of Cycloheptene.—Pyrolysis of 1.2 g at 800° resulted in 75% conversion to six products in the ratio 55:14:6:15:5:3. The products were isolated by preparative gc from the 1.0 g (84%) of pyrolysate.

The major product was identified as vinylcyclopentane: ir 3.3, 6.1, 10.1, and 11.0 μ; nmr δ 5.75 (m, 1, $C=CH$), 4.85 (m, 2, $C=CH_2$), and a broad, nine-proton resonance from 2.6 to 1.2 (ring protons); mass spectrum *m/e* (rel intensity) 96 (18), 81 (18), 68 (31), 67 (100), 54 (26), and 41 (16).

The 14% product was identified as 1,6-heptadiene: ir 3.3, 6.1, 10.1, and 11.0 μ; nmr δ 5.75 (m, 2, $C=CH$), 4.85 (m, 4, $C=CH_2$), 2.0 (m, 4, $C=CCH_2$), and 1.5 (m, 2, CH_2); mass spectrum *m/e* (rel intensity 96 (6), 81 (61), 68 (31), 67 (57), 55 (99), 54 (100), 39 (57), and 29 (76).

The other minor products were identified as cyclopentadiene, benzene, toluene, and 3-methylcyclohexane by comparison of their spectral properties with authentic samples.

1,6-Heptadiene.—The apparatus described by Bailey and King[16] was used for the pyrolysis at 525° of 17 g of 1,7-diacetoxyheptane. The crude pyrolysate was treated in the usual manner and removal of the solvent yielded 1,6-heptadiene,[17] bp 89–91°, and 7-acetoxy-1-heptene, bp 92–95° (22 mm), in a 3:2 ratio.

Pyrolysis of 1,6-Heptadiene.—A 1.2-g sample was pyrolyzed at 800° and gave 0.85 g (71%) of yellow pyrolysate. Gc analysis indicated vinylcyclopentane, 1,6-heptadiene, cycloheptene, cyclopentadiene, benzene, toluene, and 4-methylcyclohexene in a 55:12:14:3:10:3:3 ratio.

Pyrolysis of Vinylcyclopentane.—Pyrolysis of 0.7 g at 800° produced 0.55 g (79%) of pyrolysate. Gc analysis indicated the same products in the same ratios as obtained from thermolysis of 1,6-heptadiene.

Pyrolysis of Cyclopentene.—Pyrolysis of 1.1 g of cyclopentene at 800° resulted in 86% conversion to cyclopentadiene.

Pyrolysis of 4-Methylcyclohexene.—Pyrolysis of 15 mg at 800° gave 97% conversion to benzene and toluene in a 4:1 ratio.

4-Cyclooctenone.—To a cooled, stirred solution of 70 g of 4-cyclooctenol[18] in 500 ml of acetone was added dropwise 160 ml of 8 *N* chromic acid. The addition required 1.5 hr, and stirring was continued for an additional 45 min at room temperature. The mixture was poured into 500 ml of water and extracted with five 150-ml portions of pentane. The pentane extracts were combined, washed twice with water, dried, and concentrated. The residue was distilled through an annular Teflon spinning-band column to give 44 g (64%) of 4-cyclooctenone: bp 75–85° (10 mm); ir 3.3, 5.87, and 6.1 μ; nmr δ 5.65 (m, 2, $CH=CH$), 2.5 to 1.9 (m, 8, CH_2), and 1.5 (m, 2, CH_2).

Pyrolysis of 4-Cyclooctenone.—Pyrolysis of 1.1 g at 720° gave 0.9 g (82%) of pyrolysate which contained 63% 3-vinylcyclohexanone[3] and 10% octa-1,7-dien-3-one plus a host of minor products. Octa-1,7-dien-3-one was identified on the basis of spectral properties: uv max (hexane) 217 mμ (ϵ 8700); ir 5.93, 6.1, 6.2, 10.1, and 11.0 μ; nmr δ 6.2, 5.7, and 4.9 (m, 6, $CH=CH_2$), 2.53 (t, 2, J = 7 Hz, $COCH_2$), 2.0 (m, 2, $C=CCH_2$), and 1.67 (m, 2, CH_2).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.13; H, 9.58.

Pyrolysis of 3-Cyclooctenone[2] (13).—Pyrolysis of 1.3 g of **13** at 720° yielded 1.1 g (85%) of pyrolysate which contained *cis*-2-ethylidenecyclohexanone (**14**), *trans*-2-ethylidenecyclohexanone (**15**), 3-vinylcyclohexanone (**11**), and an unknown material in a 19:28:12:15 ratio as well as a plethora of minor products. Authentic samples were available.[2] The remaining compound displayed the following spectral properties consistent with assignment as **16**: uv max (hexane) 224 mμ (ϵ 12,900); ir 5.89, 6.09, 6.16, 10.1, and 11.0 μ; nmr (220 MHz) δ 6.03 (close m, *cis*-$COCH=CH$),[19] 5.8 (m, $CH=CH_2$), 5.0 (m, $CH=CH_2$), 2.4 (m, CH_2), 2.3 (m, CH_2), and 2.06 (d, $C=CHCH_3$). The presence of about 20% **18** was indicated by an ir band at 5.81 μ, nmr integral deviations, and a very characteristic nmr doublet at δ 3.06 (J = 8 Hz) attributed to a methylene group substituted by carbonyl and olefin moieties (see nmr of **13**).[2]

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.43; H, 9.63.

Upon catalytic hydrogenation this material produced 4-octanone.

Registry No.—**10**, 6925-14-0; **13**, 4734-90-1; cycloheptene, 628-92-2; *cis*-cyclooctene, 931-87-3; *cis*-cyclononene, 933-21-1; *trans*-cyclononene, 3958-38-1; *cis*-cyclododecene, 1129-89-1; *trans*-cyclododecene, 1486-75-5.

Acknowledgment.—We thank Dr. C. F. Mayer for advice and experimental assistance.

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[16] W. J. Bailey and C. King, *J. Amer. Chem. Soc.*, **77**, 75 (1955).

[17] A. Maccioni and M. Secci, *Ann. Chim. (Rome)*, **54**, 266 (1964).

[18] J. K. Crandall, D. B. Banks, R. A. Colyer, R. J. Watkins, and J. P. Arrington, *J. Org. Chem.*, **33**, 423 (1968).

[19] This assignment follows from comparison with the distinctive nmr spectra of *cis*- and *trans*-3,7-octadien-2-one: J. K. Crandall and C. F. Mayer, *ibid.*, **35**, 3049 (1970).