(tt, $J = 7, 2$ Hz, 1 H), 5.70 (ddt, $J = 17, 10, 7$ Hz, 1 H), 4.75–5.05 (m, 2 H), 4.55–4.68 (m, 1 H), 4.05–4.15 (m, 1 H), 3.30–3.50 (m, 2 H), 2.50–2.80 (m, 2 H), 1.80–2.20 (m, 2 H), 1.15–1.70 (m, 14 H); IR 3080 ($C{=}CH_2$), 1788 ($C{=}O$), 968, 910, 835 ($C{=}C$) cm^{-1}; mass spectrum *m/e* (rel intensity) 262 (M^+, 9), 219 (5), 205 (3), 191 (2), 177 (4), 163 (3), 110 (72), 43 (100).

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.53; H, 10.14.

Compound **14a**: ^1H NMR (CCl_4) δ 6.61 (tt, $J = 7, 2.5$ Hz, 1 H), 5.70 (ddt, $J = 17, 10, 7$ Hz, 1 H), 4.74–5.03 (m, 2 H), 4.60–4.74 (m, 1 H), 4.10–4.20 (m, 1 H), 3.25–3.45 (m, 2 H), 1.70–2.35 (m, 4 H), 1.15–1.70 (m, 14 H); IR 3080 ($C{=}CH_2$), 1795 ($C{=}O$), 955, 910, 837 ($C{=}C$) cm^{-1}; mass spectrum *m/e* (rel intensity) 262 (M^+, 11), 234 (4), 219 (7), 205 (7), 191 (5), 177 (9), 163 (9), 110 (78), 41 (100).

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.97; H, 10.07.

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Registry No.—**1**, 10008-73-8; **10**, 6089-09-4; **11**, 51148-68-6; **12a**, 64215-99-2; **12b**, 64216-00-8; **13a**, 64235-92-3; **13b**, 64235-93-4; **14a**, 64216-01-9; **14b**, 64216-02-0; **15a**, 112-43-6; **15b**, 52355-50-7; **15c**, 5048-44-2; **15d**, 51148-67-5; *p*-toluenesulfonyl chloride, 98-59-9; sodium cyanide, 143-33-9; methanesulfonyl chloride, 124-63-0.

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Thermolysis and Photolysis of Unsaturated Ketones. 26. Preparation of Bicyclo[2.2.2]octan-2-ones and Bicyclo[2.2.1]heptan-2-ones by Thermal Cyclization of Unsaturated Ketones. A Facile Synthesis of (+)-Camphor from (+)-Dihydrocarvone[1]

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Bicyclo[2.2.2]octan-2-ones **4a** and **4b** have been synthesized in yields of 85 and 50%, respectively, by the thermal cyclization of the appropriate 3-alkenylcyclohexanone at 390 °C. The monoterpene (+)-camphor (**10**) has been prepared in 55% yield and 90% optical purity by cyclization of (+)-dihydrocarvone (**9**) at 400 °C. An explanation for the formation in these thermolyses of a number of side products such as 2-cyclohexenones and alkylbenzenes is offered. Thermal fragmentation of bicyclo[2.2.2]octan-2-ones via a retro-Diels–Alder reaction gives an alkene and a 2-cyclohexenone, which is then converted into an alkylbenzene. It is suggested that these latter transformations may be related to the formation of some petroleum hydrocarbons from terpenoid precursors.

The thermal cyclization of unsaturated ketones has been used to prepare a wide variety of cycloalkyl ketones and cycloalkanones.[2] Bridged systems such as bicyclo[3.2.1]- and -[3.3.1]alkanes have been prepared in high yield using this technique.[2] In this report we describe the preparation of two bicyclo[2.2.2]octan-2-ones and a strained bicyclo[2.2.1]heptan-2-one, the monoterpene (+)-camphor, using this cyclization procedure. The formation of side products in these

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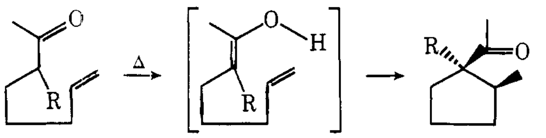
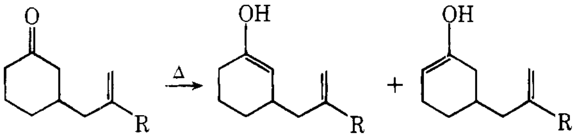
thermolysis reactions will also be rationalized.

These cyclizations proceed via the enol tautomer in a manner analogous to the intramolecular ene reaction with the enol hydrogen being transferred to the terminus of the double bond and the new carbon–carbon bond formed as illustrated in eq 1. When epimerization of the product is not possible (e.g., eq 1, R = alkyl), the stereochemistry of the product may be reliably predicted.[2]



(1)

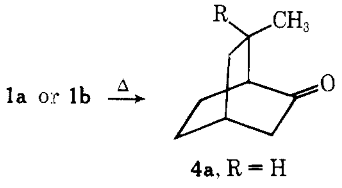
In the present investigation, employing 3-alkenylcyclohexanones such as **1**, two different enols (**2** and **3**) may be formed initially. Enol **2** would lead to a strained cyclobutyl ketone under the usual thermolysis conditions (in fact, the reverse reaction occurs in such cases[3]), while **3** should lead to the desired bridged products.



1a, R = H **2** **3**
b, R = CH_3

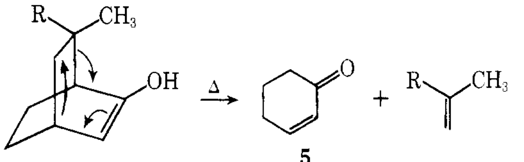
When 3-allylcyclohexanone (**1a**)[4,5] was heated for 16 h at 390 °C in the vapor phase, a crystalline product, *endo*-6-methylbicyclo[2.2.2]octan-2-one (**4a**), was formed in 85% yield along with 2-cyclohexenone (**5**, 8%). The infrared spectrum exhibited carbonyl absorption at 1725 cm^{-1}, as expected for this ring system,[6] and the NMR spectrum showed a methyl doublet at τ 9.11 and a rather sharp four-proton multiplet (4-Hz width at half height) at τ 7.91, characteristic of bicyclo[2.2.2]octan-2-ones.[7] Ketone **4a** was previously synthesized[8] by a lengthy route from a Diels–Alder adduct, and the melting point and carbonyl absorption in the infrared spectrum were in agreement with the values reported here. The endo configuration of the C_6 methyl group is that predicted from the cyclization mechanism discussed above.

Similarly, when 3-methallylcyclohexanone (**1b**)[9] was heated for 16 h at 390 °C, crystalline 6,6-dimethylbicyclo[2.2.2]-octan-2-one (**4b**) was formed in 50% yield along with 2-cyclohexenone (39%) and benzene (6%). The bicyclic ketone **4b** possessed a camphor-like odor, and its NMR spectrum exhibited a sharp four-proton multiplet at τ 7.95 (5-Hz width at half height)[7] and two singlet methyl resonances (τ 8.92 and 9.10), as anticipated for the cyclized product. **4b** has not been reported previously, but the related 4,6,6-trimethylbicyclo[2.2.2]octan-2-one exhibits singlet methyl resonances at τ 8.93, 9.08, and 9.11.[10]



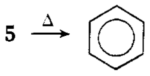
4a, R = H
b, R = CH_3

The side products formed in the thermolysis of both **1a** and **1b** deserve comment. 2-Cyclohexenone (**5**) was formed in both reactions, and we propose it originates from a retro-Diels–Alder reaction of the enol tautomer of **4** (eq 2). In the mass spectra of many bicyclo[2.2.2]octenes, the base peak is formed as a result of such a fragmentation.[11] When a pure sample of **4a** was heated under the same thermolysis conditions (390 °C, 16 h), 2-cyclohexenone was formed in low yield, showing that bicyclo[2.2.2]octan-2-ones may serve as precursors to 2-cyclohexenones. Thus, in the thermolysis of both **1a** and **1b**, there is a critical balance between the rate of cyclization of the unsaturated ketones and the rate of fragmentation of the bicyclic product (**4**). The lower yield of ketone **4b** appears to result from its more facile fragmentation and suggests that additional alkyl substitutents facilitate this retro-diene reaction. A more detailed study of this retro reaction of bicyclo[2.2.2]octan-2-ones in which the number and positions of substituents are varied could provide useful insights into both the retro and the Diels–Alder reaction itself. From the limited investigation of these two systems (**4a** and **4b**), we conclude that the more substituted ethylene is expelled in the fragmentation process. A similar preference is found in the mass spectral fragmentations of these systems.[11]



4 **5** (2)

The mechanism of formation of the aromatic hydrocarbons in these thermolyses is not obvious. We suggest that the precursors to these aromatics are the 2-cyclohexenones which are formed in the retro-diene reaction described above. Thus, benzene would be derived from 2-cyclohexenone and toluene from a methylcyclohexenone. In support of this proposal, it was found that thermolysis of 2-cyclohexenone (**5**) at 400 °C for 20 h (Table I, expt 4) resulted in a 7% conversion to benzene (**6**), with the remainder of the enone being recovered. The same conditions resulted in a 53% conversion of piperitone (**7**) to a variety of products (expt 5), the major one being *p*-cymene (**8**). These two examples confirm the cyclohexenone → benzene transformation and suggest that alkyl substituents facilitate the reaction. Further support for this conclusion will be offered later. It is important to note that these transformations involve no change in the oxidation level of the starting enone. In its simplest terms, the conversion may involve enolization of the enone followed by a series of [1,5] sigmatropic hydrogen shifts[12] to give a cyclohexadienol, which dehydrates to the aromatic system. A related transformation, conversion of cyclohexanane to 1,3-cyclohexadiene, has been investigated.[13,14]



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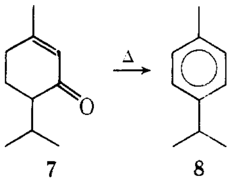


7 **8**

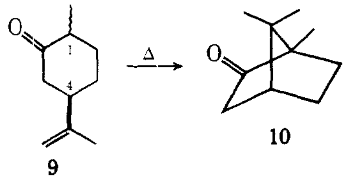
Having established that thermal cyclization was an effective method for the preparation of bicyclo[2.2.2] systems, we investigated next the possible preparation of a strained bicyclo[2.2.1]alkanone. (+)-Dihydrocarvone (**9**) was chosen as the substrate for two reasons: (i) successful cyclization of this ketone would result in a facile synthesis of (+)-camphor,[15] and (ii) the use of an optically active substrate might provide additional mechanistic information concerning these thermal reactions. **9**, prepared from (−)-carvone by reduction with lithium in liquid ammonia,[16] exists as a mixture of C_1 epimers in a 3:1 ratio. This ratio, and consequently the specific rotation of **9**, varies with the method of preparation,[17] but the mixture

Table I. Thermolysis Experiments

Expt	Ketone substrate	Registry no.	Thermolysis conditions Temp, °C	Thermolysis conditions Time, h	% conversion to products	Cyclized product, % yield	% yield of other products[a,b] 5	6	16	13	Others
1	**1a**	20498-05-9	390	16	100	**4a**, 85	8	3	4		
2	**1b**	937-44-0	390	16	95	**4b**,[g] 50	39	6			
3	**4a**	25578-20-5	390	16	5		40		40		
4	**5**	930-68-7	400	20	7			100			
5	**7**	89-81-6	400	20	53				11		50,[c] 32[d]
6	**9**	5524-05-0	400	20	80	**10**, 55			12	21	7[e]
7	**10**	464-49-3	400	20	5					20	80[f]

[a] Yields are calculated on the basis of reacted material. [b] Where total yield does not equal 100%, other minor components of undetermined structure were also detected. [c] A 3:2 mixture of 3- and 5-methyl-2-cyclohexenone, respectively. [d] *p*-Cymene. [e] A 4:3 mixture of 2- and 6-methyl-2-cyclohexenone, respectively. [f] Dihydrocarvone (**9**). [g] Registry no.: **4b**, 64235-42-3.

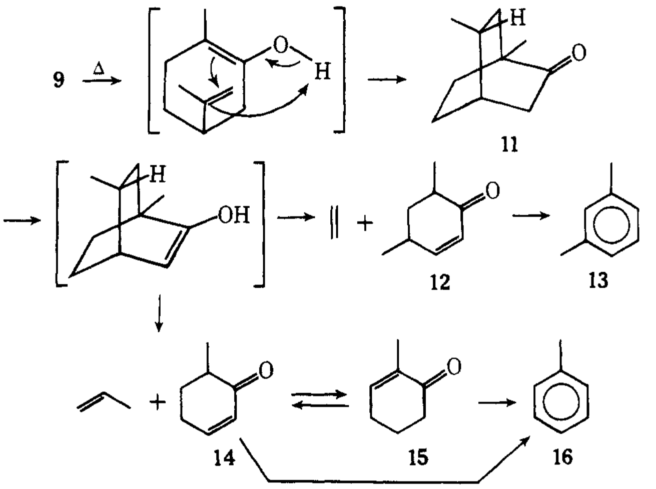
was of no concern in our synthetic approach as C_1 is involved in the enolization step prior to cyclization. Thermolysis of **9** at 400 °C for 20 h in the vapor phase resulted in an 80% conversion and gave as the major product (55%) (+)-camphor (**10**)



of 80% optical purity. Unreacted **9**, recovered by GC after the thermolysis, was found to be a 3:1 mixture of C_1 epimers and had an optical purity of only 58%. Other products that formed in the thermolysis of **9** are indicated in Table I, expt 6.

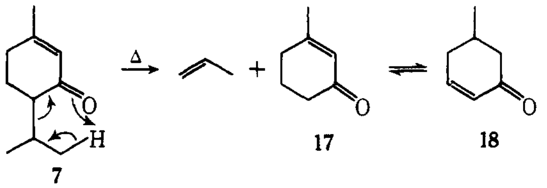
The synthesis of camphor in high yield by the BF_3-catalyzed cyclization of an enol acetate of (+)-dihydrocarvone has recently been reported, but the product was found to be racemic.[17] It was assumed that the chiral center at C_4 in **9** must have been racemized either by double bond migration or 1,2-hydrogen shifts. Under our thermolysis conditions, a similar process must have occurred but fortunately only to a minor extent. A lower optical purity of recovered **9** relative to **10** is consistent with partial racemization taking place before cyclization. This conclusion is supported also by the fact that thermolysis of (+)-camphor (**10**)[18] under the same conditions (expt 7) employed for **9** resulted in the recovery of 95% of the starting camphor of 96% optical activity.

Scheme I



The origin of the other products formed in the thermolysis of **9** is not obvious and suggests the possibility of some novel transformations. We propose that the bicyclo[2.2.2]octan-2-one **11** is the common intermediate of all five side products, **12**, **13**, **14**, **15**, and **16** (Scheme I). In the introduction it was noted that in thermal cyclization of unsaturated ketones the new carbon–carbon bond is always formed between the carbon α to the carbonyl group and the *nonterminal* end of the alkene substituent.[2] A molecular model of **9** indicates that bond formation between the α carbon and the *terminal* end of the double bond via a 6-membered transition state is not only possible but would result in the less strained bicyclo[2.2.2] system **11**, as compared with the bicyclo[2.2.1] system in **10**. Apparently, under the thermolysis conditions required to effect the reaction of **9**, the enol of **11** (Scheme I) is converted completely to enones **12** and **14** via retro-Diels–Alder reactions. Subsequently, **12** is transformed to the major side product *m*-xylene (**13**) while **14** undergoes thermal isomerization to **15**, and then both **14** and **15** are partially converted to toluene (**16**).[19] Our study of the bicyclo[2.2.2]octan-2-ones described above provides precedents for both the fragmentation of **11**[20] and the conversion of the resultant enones to alkylated benzenes. The fact that dimethylcyclohexenones (e.g., **12**) were not isolated (only the transformation product **13**) while methylcyclohexenones **14** and **15** were isolated provides additional support for the suggestion that alkyl substituents facilitate the conversion to the substituted benzenes.

Thermal isomerization of enone **14** to **15**, possibly via a [1,5] sigmatropic hydrogen shift in the enol of **14**, further illustrates the lability of the double bonds at these temperatures. An additional example of this type of enone isomerization was found upon thermolysis of piperitone (**7**) (Table I, expt 5). In addition to the 32% yield of *p*-cymene described above, it was expected that a McLafferty-type rearrangement in **7** would yield **17**. Instead, a mixture of **17** and **18** was formed in 50% yield of converted material, with **18** arising by thermal isomerization of **17**.



In conclusion, we have shown that thermolysis of 3-alkenylcyclohexanones at 390–400 °C is an effective method for the preparation of substituted bicyclo[2.2.2]octan-2-ones and bicyclo[2.2.1]heptan-2-ones. Specifically, we have synthesized the monoterpene (+)-camphor in good yield and high optical purity. In addition, we believe that certain other transformations described here may be related to the formation of petroleum hydrocarbons. Terpenoids have long been thought to be important precursors of petroleum products,[21] but the details of these transformations have not been clear in most instances.[22] In this report we have shown that monoterpenes (e.g., **7** and **9**) may be converted by thermolysis[23,24] to toluene and/or *m*-xylene, which are two of the most abundant aromatic hydrocarbons in petroleum.[25]

Experimental Section

Melting points were determined on a Mettler FP 51 automatic apparatus, infrared spectra were recorded on a Perkin-Elmer 457G spectrophotometer, ultraviolet spectra on a Unicam SP 1800 spectrophotometer, and mass spectra on a Varian M-66 spectrometer operating at 70 eV. Optical rotations were determined on a Perkin-Elmer 141 automatic polarimeter at 25 °C with absolute ethanol as the solvent, and ^{1}H NMR spectra were recorded on a Perkin-Elmer R12A 60-MHz spectrometer using the internal standard tetramethylsilane (τ 10.0) and the following designations: s, singlet; d, doublet; m, multiplet. Gas chromatographic (GC) analyses and collections were done on an Aerograph Model A-90P with hydrogen as the carrier gas and the following columns: A, 3.5 m × 8 mm, 20% Carbowax 20M on 45–60 mesh Chromosorb P; B, 4.0 m × 8 mm, 20% SE30 on 45–60 mesh Chromosorb P. Peak areas were determined by triangulation and were not corrected for differences in thermal response.

The thermolyses were conducted in a 500-mL evacuated (<0.025 Torr) glass reactor, using the apparatus previously described.[26] The samples to be thermolyzed were routinely collected by preparative GC prior to reaction, and the sample size was normally 300–350 mg. The thermolysis products were immediately distilled into a cold finger cooled in liquid nitrogen and analyzed. In none of the thermolyses described was there any significant polymerization or tar formation, and thus the product recoveries were nearly quantitative. Where the thermolysis products were known compounds, their structures were confirmed by comparison of NMR, IR, and GC retention times on both columns A and B with authentic samples. The per cent conversion and the product distribution of the compounds thermolyzed are summarized in Table I.

***endo*-6-Methylbicyclo[2.2.2]octan-2-one (4a).** A 320-mg sample of 3-allylcyclohexanone (**1a**)[4,5] was placed in the thermolysis reactor at 390 °C for 16 h. Distillation of the product gave 300 mg of a pale yellow oil which darkened after several hours at room temperature. GC analysis (column A, 176 °C; column B, 145 °C) gave the product distribution indicated in Table I, expt 1. The major peak was collected by preparative GC and identified as **4a**: mp 52 °C (lit.[8] 50–52 °C); IR (neat) 2930, 2870, 1725, 1455, 1095 cm^{-1}; IR (CCl$_4$) 1729 cm^{-1} (lit.[8] 1729 cm^{-1}); NMR (CCl$_4$) τ 9.11 (3 H, d, J = 6.0 Hz), 8.89 (1 H, m), 8.28 (4 H, m), 8.05 (2 H, m), 7.91 (4 H, m, 4-Hz width at half-height); mass spectrum, *m/e* (rel intensity) 138 (M$^+$, 100), 123 (10), 95 (4), 94 (9).

Anal. Calcd for $C_9H_{14}O$: *m/e* 138.104. Found: *m/e* 138.104.

6,6-Dimethylbicyclo[2.2.2]octan-2-one (4b). A 200-mg sample of 3-methallylcyclohexanone (**1b**)[9] was thermolyzed at 390 °C for 16 h and distilled to give a pale yellow oil which was analyzed by GC (column A, 185 °C; column B, 155 °C) to give the product distribution reported in Table I, expt 2. The major product, which had a retention time slightly shorter than **1b** on column B, was collected on this column. It was found to possess a camphor-like odor and was identified as **4b**: mp 117 °C; IR (melt) 2920, 2870, 1725, 1450, 1220 cm^{-1}; IR (CCl$_4$) 1730 cm^{-1}; NMR (CCl$_4$) τ 9.10 (3 H, s), 8.92 (3 H, s), 8.15–8.68 (6 H, m), 7.95 (4 H, m, 5-Hz width at half-height); mass spectrum, *m/e* (rel intensity) 152 (M$^+$, 100), 138 (25), 137 (22), 109 (5), 95 (8).

Anal. Calcd for $C_{10}H_{16}O$: *m/e* 152.120. Found: *m/e* 152.123.

(+)-Camphor (10). (+)-Dihydrocarvone (9), α_D +10.9° (*c* 3.0), was prepared[16] from (−)-carvone, α_D −62° (Fluka), and purified by preparative GC. A 350-mg sample of 9 was thermolyzed at 400 °C for 20 h and analyzed by GC (Table I, expt 6). All the major peaks were collected by GC and compared with authentic samples. The synthetic (+)-camphor was found to have α_D +32° (*c* 3.3), while a natural (+)-camphor sample which was collected and analyzed in the same number was found to have α_D +40° (*c* 3.8). The recovered **9** at the end of the thermolysis was found to have α_D +6.3° (*c* 1.9).

References and Notes

(1) This research was accomplished while G. L. L. was on sabbatical leave at Université de Paris-Sud. A preliminary account of a portion of this work has been published: G. L. Lange and J. M. Conia, *Nouv. J. Chim.*, **1**, 189 (1977).

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(4) Prepared as described previously[5a] except that allyllithium was formed from the reaction of allyl phenyl ether with lithium.[5b]

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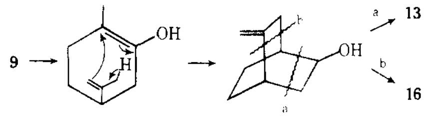
(18) Thermolysis of camphor at 800 °C gives a number of products: T. Sato, K. Murata, A. Nishimura, T. Tsuchiya, and N. Wasada, *Tetrahedron*, **23**, 1791 (1967).

(19) An ene reaction of the enol of **9** followed by fragmentation and dehydrogenation also would account for the formation of **13** and **16** but not **14** and **15**. A study is under way to distinguish between these possible mechanisms.



(20) In the fragmentations of **4a** and **4b** the more substituted ethylenes were expelled, while with **11** approximately the same amounts of ethylene and propylene were expelled to give **13** (21%) and **14** + **15** + **16** (19%), respectively.

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