Synthesis of *gem*-Dimethylcycloheptadienes *via* Homoallylic Ring Expansion

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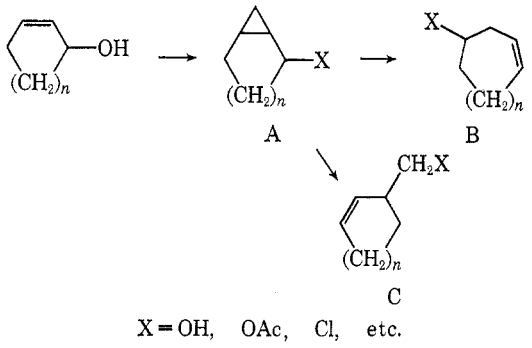
Several synthetic routes to *gem*-dimethylcycloheptadienes involving cyclopropanation of 5,5-dimethyl-2-cyclohexenol (**4**) coupled with homoallylic ring expansion have been investigated. Satisfactory conversions were effected either by bromination of *cis*-4,4-dimethylbicyclo[4.1.0]heptan-2-ol (*cis*-**5**) with 48% hydrogen bromide followed by base-promoted dehydrobromination or by acetylation of *cis*-**5** followed by pyrolysis. The diene product distributions in the former route are subject to both kinetic and thermodynamic control and the importance of these factors is discussed with respect to several base–solvent systems.

There are many examples of the acid-catalyzed opening of cyclopropylcarbinols to afford acyclic olefins,[1] sometimes in a highly stereoselective manner.[2,3] In addition, the conversion of cyclic allylic alcohols to the corresponding cyclopropyl alcohols, coupled with acid-catalyzed opening of the latter (to give type B products), has been shown to be a useful method for ring

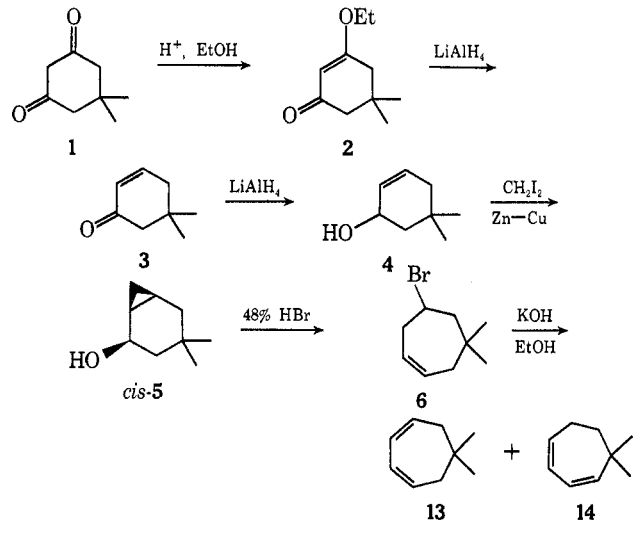


expansion.[3] However, depending on the conditions, bicyclic products (type A) may be formed[4] or cleavage may occur at a perimetrical cyclopropyl bond to give type C products.[5] Because of the potential synthetic utility of these reactions and because of a need for several previously unknown *gem*-dimethyl-substituted cycloheptadienes, we decided to employ a route which would further extend the scope of homoallylic ring expansion reactions.

Results and Discussion

The reaction sequence which was employed with the most success is outlined in Scheme I. All of the reac-

SCHEME I



tions occur in good yield (>70%) to afford reasonably pure products (>92% in each case); the overall yield of cycloheptadienes is ~40%.

5,5-Dimethyl-2-cyclohexenone (**3**) was prepared from 5,5-dimethyl-1,3-cyclohexanedione (dimedon or methone) (**1**) by the method of Frank and Hall.[6] Greatly increased yields (~90%) can be obtained with the use of fresh reducing agent in the reduction of 3-ethoxy-5,5-dimethyl-2-cyclohexenone (**2**) (see Experimental Section).

The third step, which entails a lithium aluminum hydride reduction of the α,β-unsaturated ketone **3**, must be carefully controlled in order to obtain a good yield of reasonably pure allylic alcohol **4**. We have obtained satisfactory conversions by treating **3** with a 10% equiv excess of fresh reducing agent for 20 min. When **3** is stirred for 8 hr with a twofold excess of lithium aluminum hydride the product mixture contains a substantial quantity of a saturated alcohol, 3,3-dimethylcyclohexanol. The use of sodium borohydride leads to even more extensive reduction of the double bond. Similar behavior of α,β-unsaturated

(1) For reviews, see (a) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem., Int. Ed. Engl.*, **7**, 577 (1968); (b) M. Hanack and H.-J. Schneider, *ibid.*, **6**, 666 (1967); *Fortschr. Chem. Forsch.*, **8**, 554 (1967); (c) H. G. Richey, Jr., in "Carbonium Ions," Vol. 3, G. A. Olah and P. von R. Schleyer, Ed., Wiley, New York, N. Y., 1969.

(2) S. F. Brady, M. A. Ilton, and W. S. Johnson, *J. Amer. Chem. Soc.*, **90**, 2882 (1968).

(3) (a) M. Gašić, D. Whalen, B. Johnson, and S. Winstein, *ibid.*, **89**, 6382 (1967); (b) D. Whalen, M. Gašić, B. Johnson, H. Jones, and S. Winstein, *ibid.*, **89**, 6384 (1967).

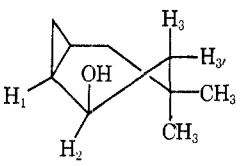
(4) For examples involving bicyclo[4.1.0]heptyl products, see (a) W. G. Dauben and L. E. Friedrich, *Tetrahedron Lett.*, 1735 (1967); (b) J. Tadanier, *J. Org. Chem.*, **31**, 2124 (1966); (c) L. Birladeanu, T. Hanafusa, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 2315 (1966); (d) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *ibid.*, **88**, 2316 (1966); (e) H. L. Goering and K. E. Rubenstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., 1966, p K11; (f) S. W. Pelletier, S. Nakamura, and Y. Shimizu, *Chem. Commun.*, 727 (1966); (g) A. C. Cope, C. H. Park, and P. Scheiner, *J. Amer. Chem. Soc.*, **84**, 4862 (1962).

(5) For examples related to those in ref 4 see ref 4a, b, and f and (a) E. C. Friedrich, *J. Org. Chem.*, **34**, 528 (1969); (b) H. Laurent, H. Müller, and R. Wiechert, *Chem. Ber.*, **99**, 3836 (1966); (c) Y. Hikino and P. de Mayo, *Chem. Commun.*, 550 (1965); (d) M. Julia, S. Julia, T. S. Yu, and C. Neuville, *Bull. Soc. Chim. Fr.*, 1381 (1960), and earlier papers; (e) W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, **34**, 2512 (1969).

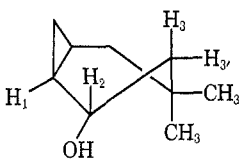
(6) R. L. Frank and H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **72**, 1645 (1950).

carbonyl compounds has been noted by other workers.[7,8]

A cyclopropyl ring was next introduced adjacent to the hydroxyl group by treatment of **4** with methylene iodide and zinc–copper couple.[4g,9] By analogy with the majority[9b–d] of previous reports of the cyclopropanation of 2-cyclohexenol,[4g,9b–d] the product was expected to be essentially all cis isomer. This is confirmed by the nmr spectrum of the single bicyclo[4.1.0]heptanol product (*cis*-**5**), particularly by the splitting of the C_2 proton at τ 5.82 which is a five-line multiplet (two overlapping doublets of doublets) with a line separation of 5.8 Hz. Thus H_1, H_3, and $H_{3'}$ are all



cis-**5**

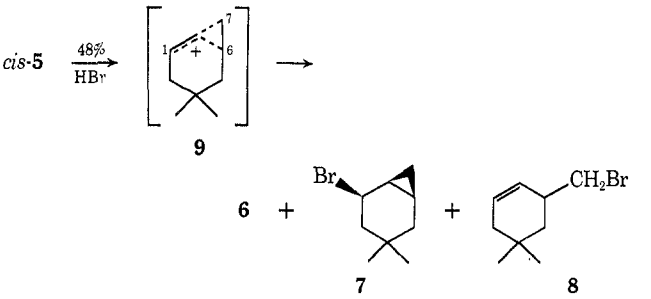


trans-**5**

coupled reasonably strongly with H_2 (see Experimental Section). On the other hand, the signal for H_2 (τ 5.93) in the trans isomer of **5** (*trans*-**5**)[10] is an apparent triplet (*i.e.*, overlapping doublets) with a line separation of 5.3 Hz. Since the dihedral angle between H_1 and H_2 is ~40° in *cis*-**5** and ~80° in *trans*-**5** (from Dreiding models) the stereochemical assignments are consistent with the much larger value of J_{12} in *cis*-**5** (5.8 Hz as opposed to <1 Hz in *trans*-**5**).[11]

Under favorable reaction conditions (0.5 hr in ether at reflux) *cis*-**5** is obtained in ~70% yield contaminated with only minor amounts of unchanged **4** and a second product. If the reaction is allowed to proceed for longer periods the latter compound can constitute a significant portion of the product mixture. It has been identified as 3-iodomethyl-5,5-dimethylcyclohexene, primarily on the basis of the mass (molecular ion at *m/e* 250.022) and nmr [doublet at τ 6.92 (2 H, iodomethyl, J = 6 Hz)] spectra.[10] We are currently investigating the mechanism of this novel reaction.

The critical step in this reaction sequence is the one involving ring expansion. We have found that the conversion of *cis*-**5** to 6-bromo-4,4-dimethylcycloheptene (**6**) can be effected in >90% yield with only slight contamination by two isomeric products (**7** and **8**) by stirring with 48% hydrogen bromide at room temperature for 6 hr.[12] The bromo and cyclopropyl groups are cis to each other in **7** since the C_2 proton (–CHBr–) signal at τ 5.2 is a broadened five-line pattern similar to that in *cis*-**5** (*vide supra*). This

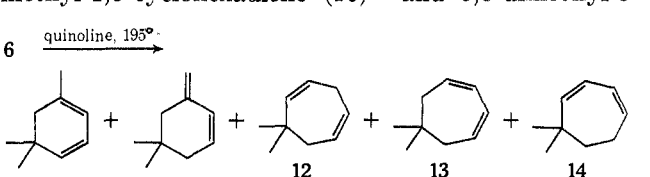


isomer is actually the major product for short reaction times (10 min or less) but is converted to **6** upon stirring with acid. In addition, the third isomer (**8**) is the major product after about 3 days at room temperature (or after 15 min at 195°).[10]

If one assumes that the reaction proceeds *via* the delocalized homoallylic ion **9**, in which the positive charge is located primarily at C_1, C_6, and C_7,[3a,13,14] it can be seen that products resulting from attack of bromide at each of these positions are observed.[15] This reaction represents an interesting example of the use of both kinetic and thermodynamic control for synthetic purposes since it is necessary to convert the initially formed but least stable isomer (**7**) into the desired product (**6**) without the latter in turn being converted into the most stable isomer (**8**).

We have investigated the dehydrobromination of **6** by employing several base systems which vary over a wide range of base strength. These include a weak base (quinoline), a medium-strength base (potassium hydroxide in ethanol), and a strong base (potassium amide in liquid ammonia).[16]

On heating **6** with quinoline at 195° for 20 min a 72% yield of at least five C_9H_{14} isomers is obtained (Table I). These isomers were isolated by gas chromatography and identified on the basis of spectroscopic evidence (see Experimental Section). Two of the isomers were identified as six-membered-ring dienes, *viz.*, 1,5,5-trimethyl-1,3-cyclohexadiene (**10**)[17] and 5,5-dimethyl-3-



(7) (a) M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, *Bull. Soc. Chim. Fr.*, 1042 (1952), and references cited; (b) J. W. Wheeler and R. H. Chung, *J. Org. Chem.*, **34**, 1149 (1969), and references cited; (c) W. L. Dilling and R. A. Plepys, *Chem. Commun.*, 417 (1969); (d) H. C. Brown and H. M. Hess, *J. Org. Chem.*, **34**, 2206 (1969), and references cited. The greater amount of double bond reduction which we observe with sodium borohydride (relative to lithium aluminum hydride) is in accord with the results in the latter three papers, and in (e) F. Sondheimer, M. Velasco, E. Batres, and G. Rosenkranz, *Chem. Ind. (London)*, 1482 (1954); (f) H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Amer. Chem. Soc.*, **83**, 1391 (1961). (g) See K. E. Wilson, R. T. Seidner, and S. Masamune, *Chem. Commun.*, 213 (1970), for a potentially useful reagent.

(8) It was previously reported [A. S. Dreiding and J. A. Hartman, *J. Amer. Chem. Soc.*, **75**, 3723 (1953)], that **4** is obtained from the lithium aluminum hydride reduction of **1**. However, in our hands this procedure afforded a 2:1 mixture of **4** and 3,3-dimethylcyclohexanol. We have not investigated this reaction in detail but it may be possible, by using less reducing agent, to obtain reasonably pure **4** in good yield by this more convenient route.

(9) (a) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959); (b) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963); (c) S. Sawada, K. Takehana, and Y. Inouye, *J. Org. Chem.*, **33**, 1767 (1968); (d) J. H.-H. Chan and B. Rickborn, *J. Amer. Chem. Soc.*, **90**, 6406 (1968).

(10) S. W. Staley and F. L. Wiseman, Jr., to be published.

(11) H. Conroy, *Advan. Org. Chem.*, **2**, 265 (1960).

(12) This is an extension of the method of M. Julia, S. Julia, and R. Guégan, *Bull. Soc. Chim. Fr.*, 1072 (1960).

(13) P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).

(14) It should be recognized, however, that several closely related, but different, ions may be involved. See ref 1b, 5e, and K. B. Wiberg and A. J. Ashe, III, *J. Amer. Chem. Soc.*, **90**, 63 (1968).

(15) We, of course, are not able to observe migration of the cyclopropyl group, as has been observed or suggested by others (ref 4a, b and f and 5b and c) since this merely interconverts enantiomeric ions in the present case.

(16) For a listing of base strengths, see J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, pp 219–21.

(17) This compound may contain a small amount of 2,6,6-trimethyl-1,3-cyclohexadiene. At equilibrium **10** has been found to predominate over the latter isomer by a factor of 5:2 in potassium-*t*-butoxide–hexamethylphosphoramide at 25°: S. W. Staley, W. L. Maloy, and J. P. Erdman, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968, p P129.

TABLE I

PRODUCT DISTRIBUTIONS FOR THE BASE-PROMOTED DEHYDROBROMINATION OF 6-BROMO-4,4-DIMETHYLCYCLOHEPTENE (6) IN VARIOUS BASE–SOLVENT SYSTEMS

Product	Quinoline, 195°, 20 min[a]	KNH_2–NH_3, 25°, 5 min[a]	KOH–EtOH, 80°, 30 min[a]
10[b]	26.5	0	2[c]
11	13.5	0	1[c]
12	12	15	0
13	25	30	89
14	23	55	8

[a] Approximate percentage of isolated product. [b] Probably contains ~15% 2,6,6-trimethyl-1,3-cyclohexadiene. [c] Probably arises from ~2–3% 3-bromomethyl-5,5-dimethylcyclohexene present as an impurity in 6.

methylenecyclohexene (**11**). Both compounds exhibit ir, uv, and mass spectra which are essentially identical with those of authentic samples.[18]

The remaining three isomers are cycloheptadienes; **12** is nonconjugated, as shown by its uv spectrum which displays only end absorption, whereas **13** and **14** are both conjugated [λ_{max}^{hexane} 246 (ϵ 6160) and 248 nm (13,200), respectively].[19] The latter two isomers are readily distinguished by their nmr spectra since that of **13** indicates four allylic protons whereas that of **14** shows two allylic and two methylene protons.

The presence of a large quantity of six-membered-ring dienes in the product mixture is of considerable interest. Control experiments which employed conditions similar to those used for dehydrobromination have established that the cycloheptadienes are not converted to the C_6-ring dienes, although the reverse process does occur. Diene **11** is the major C_6-ring product in low conversion dehydrobrominations of **6** (Table II), thereby indicating

TABLE II

DEHYDROBROMINATION OF 6-BROMO-4,4-DIMETHYLCYCLOHEPTENE (6) WITH QUINOLINE

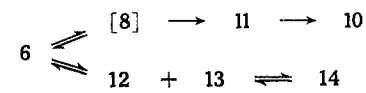
Reaction time	Percentage dehydrobromination	Product distribution[a] 10[b]	11	12	13	14
30 sec	10	0	25	10	58	7
1 min	60	2	26	14	37	21
2 min	87	8	21	16	29	26

[a] Approximate percentage (of the isomers listed) as measured by gas chromatography; obtained by placing a 20% (v/v) solution of **6** in quinoline (at 25°) in an oil bath at 215° for the indicated length of time. [b] May contain some 2,6,6-trimethyl-1,3-cyclohexadiene.

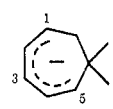
that this isomer is formed initially and then converted to **10**.[20] Since we have shown that bromide **6** is isomerized to bromide **8** in 48% hydrogen bromide or in sulfuric acid–dioxane,[10] the latter isomer is a reasonable intermediate in the formation of **11** (Scheme II). The ratio of **10** to **11** (Table I) is essentially that expected at equilibrium.[18b]

1,2-Dehydrobromination of **6** would lead to **12** and **13** and these are the major cycloheptadiene products in the initial stages of the reaction (Table II). The nonconjugated isomer is substantially less stable than **13** and **14** (*vide infra*) and therefore is formed in a kinetically controlled process. In contrast, the ratio of **13** to **14** is approximately that expected at equilibrium.[10] There are several possible mechanisms for the interconversion of the latter two isomers; these include catalysis by quinoline hydrobromide–quinoline, and a concerted [1,5]-suprafacial sigmatropic migration of hydrogen.[21]

SCHEME II



Dehydrobromination with the strongest base, potassium amide in liquid ammonia, affords only cycloheptadienes as products but the recovery is rather poor (27%). In this case potassium cycloheptadienyl anion (**15**) is an intermediate and the distribution of products



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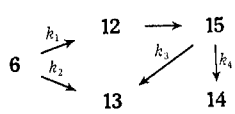
is governed by the relative rates of protonation at C_1, C_3, and C_5 upon quenching (accompanied, perhaps, by some isomerization during the brief quenching process). Anion **15** is known to be present under these conditions since it can be generated in high yield (by adding a mixture of **12**, **13**, and **14** to a twofold excess of potassium amide in liquid ammonia) and directly observed by nmr spectroscopy.[10]

The highest yield of cycloheptadienes (78%) was obtained by heating **6** in potassium hydroxide–ethanol at reflux (~95°); the product was isolated as an 11:1 mixture of **13** and **14**. Since **14** cannot arise directly from **6** by 1,2 elimination and since it was established that **13** and **14** are not interconverted to a significant extent under the reaction conditions, the most reasonable pathway for the formation of the latter isomer is *via* **12** (Scheme III). This mechanism is supported by

SCHEME III



the fact that **12** in a mixture with **13** and **14** is converted virtually completely into the latter two isomers when treated under the reaction conditions (Table V). Since there was little material loss (as shown by use of an internal standard) this establishes that **12** is substantially less stable than **13** and **14**,[22] and allows one to estimate that k_3/k_4 = ~2.3. With this figure and the data in Table I, k_2/k_1 (in potassium hydroxide–ethanol) can be estimated to be 3. The greater value of

(18) (a) H. Pines and R. H. Kozlowski, *J. Amer. Chem. Soc.*, **78**, 3776 (1956); (b) S. W. Staley and J. P. Erdman, unpublished results.

(19) 1,3-Cycloheptadiene has $\lambda_{max}^{isooctane}$ 248 nm (ϵ 7400): E. Pesch and S. L. Friess, *ibid.*, **72**, 5756 (1950).

(20) We have also shown by a control experiment that this isomerization occurs in quinoline hydrobromide–quinoline at 200°.

(21) (a) This isomerization can occur either as in ref 20 or in pentane at 200°. (b) For a similar thermal rearrangement, see V. A. Mironov, O. S. Chizhov, Ia. M. Kimelfeld, and A. A. Akhrem, *Tetrahedron Lett.*, 499 (1969).

(22) (a) The heat of hydrogenation of 1,4-cycloheptadiene is 6.0 kcal/mol greater than that of 1,3-cycloheptadiene (both in acetic acid at 25°): R. B. Turner, personal communication. (b) 1,4-Cycloheptadiene is isomerized to 1,3-cycloheptadiene in refluxing potassium ethoxide–ethanol: W. von E. Doering and G. Schröder, cited by W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

k_2 relative to k_1 may be due in part to the fact that the respective transition states reflect the stabilities of the products. However, the role of steric factors in these two processes is unclear at the present time.

It can be seen that both kinetic and thermodynamic control of the cycloheptadiene product mixtures are operative. The type of control for a given product varies with the dehydrobrominating conditions; the results are summarized in Table III.

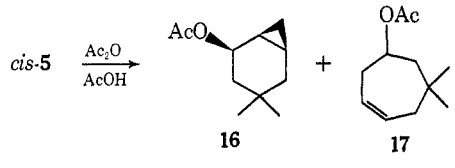
TABLE III
TYPE OF PRODUCT CONTROL (K = KINETIC, T = THERMODYNAMIC) FOR THE BASE-PROMOTED DEHYDROBROMINATION OF 6-BROMO-4,4-DIMETHYLCYCLOHEPTENE (6)

Product	Quinoline	KNH_2–NH_3[a]	KOH–EtOH
12	K	K	T
13	T	K	K + T[b]
14	T	K	T

[a] Some equilibration may occur during the quenching process. [b] Kinetic control predominates; 12, but not 14, is isomerized to 13.

Alternate Routes.—Two other routes from alcohol *cis*-5 to cycloheptadienes 12–14 were explored. Although they were not studied as extensively as the bromination–dehydrobromination route, it is nevertheless of value to discuss our initial results.

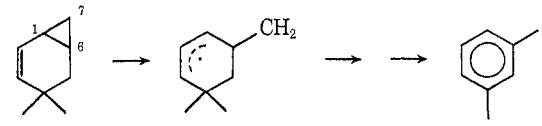
Behavior analogous to that observed on treatment with 48% hydrogen bromide was noted when *cis*-5 was heated at reflux with acetic anhydride–acetic acid. When the reaction is allowed to proceed for 6 hr a 6:4 mixture of acetates 16 and 17 is obtained as the major product, but after 26 hr the ring expanded acetate (17) predominates by a factor of >20. This represents yet another example of kinetic *vs.* thermodynamic control in this system.



When ~92% pure 17 is pyrolyzed at 516° in a flow system a >50% yield of a mixture which contains 11% 12, 37% 13, and 37% 14 is obtained. The first two isomers are probably formed by concerted cis elimination of acetic acid; 14 is undoubtedly formed from 13 *via* a 1,5 hydrogen shift mechanism.[21b] In contrast, pyrolysis of a sample which was predominantly a 3:2 mixture of 16 and 17 gave *m*-xylene as the major product. This could arise by pyrolysis of a primary product, 4,4-dimethylbicyclo[4.1.0]hept-2-ene (18) (*vide infra*).

When alcohol *cis*-5 was heated at 230° in the presence of a catalytic amount of *p*-toluenesulfonic acid, complex mixtures of products were obtained. The product ratios varied somewhat between two runs but the yield of cycloheptadienes never exceeded 20% of the isolated products. This reaction therefore appears to have much less synthetic potential than the two which have already been discussed (dehydrobromination and acetate pyrolysis).

The major component in the product mixtures from dehydration of *cis*-5 was identified as 18 on the basis of its nmr spectrum. The presence of this compound allowed us to test the supposition that the *m*-xylene obtained from the pyrolysis of a 3:2 mixture of acetates 16 and 17 is formed from 18 (which would arise by pyrolysis of 16). Thus, when a dehydration product mixture containing 45% 18 was heated in a sealed tube at 320° or in a flow system at 490°, *m*-xylene comprised about half the product mixture. Apparently cleavage occurs predominantly at C_1–C_7 instead of at C_1–C_6.[23]



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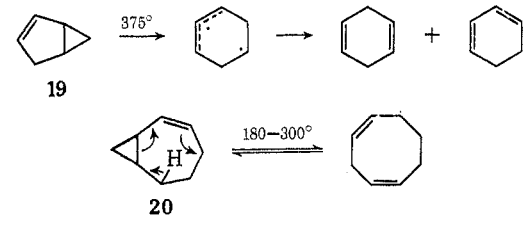
These results can be contrasted with those for bicyclo[3.1.0]hex-2-ene (19)[24] and bicyclo[5.1.0]oct-2-ene (20).[25] It can be rationalized that the biradical mechanism suggested[24b] for 19 is less likely in the case of 18



because the bridge C–C bond is less strained in the latter compound. Furthermore, a concerted 1,5 hydrogen migration is more probable for 20 than for 18 since there will be better overlap (less strain) in the activated complex for the former compound.[26]

Summary

It is apparent that acid-catalyzed ring expansion of α-cyclopropyl alcohol *cis*-5 followed by base-promoted dehydrobromination of bromide 6 constitutes a convenient high-yield synthesis of *gem*-dimethylcycloheptadienes. Considerations of kinetic and thermodynamic control are important in both of the key steps. Particular attention must be paid to this point if a specific cycloheptadiene is desired since different bases afford markedly different product ratios.

Experimental Section

General Comments.—Infrared (ir) spectra (neat) were obtained in a 0.025-mm sodium chloride or potassium bromide cell on a Perkin-Elmer 337 instrument; nuclear magnetic resonance (nmr) spectra of ~10% solutions in carbon tetrachloride with internal tetramethylsilane were recorded on a Varian A-60A spectrometer; ultraviolet (uv) spectra of Spectrograde hexane solutions were obtained on a Cary 14 instrument, and mass spectra were recorded at 70 eV on a Varian M-66 mass spectrometer. Boiling points are uncorrected. Elemental analyses were performed by Dr. Franz Kasler of the University of Maryland.

Analyses by gas chromatography (gc) were performed on an Aerograph 1200 (1/8-in. columns, flame ionization detector) or A90-P3 (1/4-in. columns, thermal conductivity detector) instru-

(23) For related reactions, see ref 18a and J. A. Berson and E. S. Hand, *J. Amer. Chem. Soc.*, **86**, 1978 (1964).

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ment and are not corrected for response factors. Gc columns were generally made with copper tubing. The following were employed (outside diameter and length are given): CW20M-1, 15% Carbowax 20M on 80–100 acid washed and silanized (AW-S) Chromosorb P (1/8 in. × 5 m); CW20M-2, 8% Carbowax 20M on 100–120 AW-S Chromosorb P (1/8 in. × 3 m); CW20M-3, same as CW20M-1 except 1/4 in. × 1.5 m; m; CW20M-4, 20% Carbowax 20M on 60–80 Diatoport S (1/4 in. × 5 m); SE30-1, 5% SE-30 silicone oil on 60–80 Chromosorb W (1/8 in. × 1.7 m, stainless steel); SE30-2, 20% SE-30 silicone oil on 60–80 AW-S Chromosorb P (1/8 in. × 1.5 m, stainless steel); TCEP-1, 15% 1,2,3-tris(2-cyanoethoxy)propane on 100–120 AW-S Chromosorb P (1/4 in. × 2 m); TCEPE-1, 7% tetracyanoethoxypentaerithritol on 80–100 AW-S Chromosorb P (1/8 in. × 0.6 m).

3-Ethoxy-5,5-dimethyl-2-cyclohexenone (**2**) was prepared by the method of Frank and Hall[6] in 98% yield, bp 97–105° (2 mm) [lit.[6] bp 93° (1 mm)]. The nmr spectrum displays signals at τ 4.79 (s, 1, C=C-H), 6.08 (q, 2, J = 7 Hz, OCH_2), 7.77 (s, 2, CH_2), 7.92 (s, 2, CH_2), 8.65 (t, 3, J = 7 Hz, CH_3), and 8.93 (s, 6, CH_3); no other peaks were observed.

5,5-Dimethyl-2-cyclohexenone (**3**) was prepared as described previously[6] except that a 15% equiv excess of fresh lithium aluminum hydride was employed. A 90% yield of material with bp 40–48° (1.6 mm) [lit.[6] bp 75° (15 mm)] was obtained: nmr τ 3.17 (doublet of triplets, 1, J = 10 and 4 Hz, respectively, CH=CH-CH_2), 4.08 (doublet of triplets, 1, J = 10 and 2 Hz, respectively, CH=CH-CH_2), 7.70 (doublet of doublets, 2, J = 2 and 4 Hz, CH_2), 7.80 (s, 2, CH_2), and 8.93 (s, 6, CH_3); no other signals were detected. Yields of 45–55% (similar to that reported by Frank and Hall[6]) were obtained when reducing agent which had been on the shelf for months in an inadequately sealed container was used.

5,5-Dimethyl-2-cyclohexenol (**4**).—5,5-Dimethyl-2-cyclohexenone (25 g, 0.20 mol) was added over 0.5 hr to a cooled suspension of 2.2 g (0.23 equiv) of fresh lithium aluminum hydride in 300 ml of dry ether. The reaction mixture was then heated at reflux for 20 min, cooled, and treated with water followed by saturated aqueous ammonium chloride. The aqueous layer was extracted twice with ether and the combined ether layers were dried over anhydrous magnesium sulfate. The ether was distilled and the residue vacuum distilled to afford 22.6 g [bp 86–88° (17 mm)] of 93% pure **4** (83% yield).[7b] This material was shown to contain a trace of **3** by gas chromatography (gc) (column CW20M-3 at 100°) and ir (small carbonyl band at 1698 cm^{-1}) and ~6% 3,3-dimethylcyclohexanol (**21**) by gc and nmr. After purification by gc on this same column [retention time (rt) relative to **21** was ~1.2], **4** gave the following spectral data: ir 3340, 3035, 1650, 1385, 1370, 1282, 1089, 1035, 1000, 934, 800, and 725 cm^{-1}; nmr τ 4.39 (s, 2, C=CH), 5.9 (broad m, 1, CHOH), 6.95 (s, 1, COH), 8.21 (m, 2, C=C-CH_2), 8.50 (d, 1, J = 8.5 Hz, CH_2), 8.75 (1, broadened d, J = 3.5 Hz, CH_2), 9.00 (s, 3, CH_3), and 9.10 (s, 3, CH_3).

Anal. Calcd for $C_8H_{14}O$: C, 76.15; H, 11.17. Found: C, 75.88; H, 10.92.

When 20.1 g (0.16 mol) of **3** was added to 4.7 g (0.5 equiv, threefold excess) of lithium aluminum hydride in 250 ml of dry ether, stirred at reflux for 41 hr, and worked up as above (except that quenching was effected with water followed by dilute sulfuric acid), 20 g of product was obtained. This was shown by nmr to be a 1:1 mixture of **4** and **21**.

When **3** was stirred with a fivefold excess of saturated sodium borohydride in 0.2 *N* sodium hydroxide–ethanol for 20 hr at room temperature, a crude product was obtained whose nmr showed no vinyl hydrogens.

A sample of **21** which was purified by gc has ir and nmr spectra which agree with reported data:[27] ir 3340, 1380, 1365, 1062, 1022, 970, 944, 923, 899, 852, and 812 cm^{-1}; nmr 6.0–6.7 (m, 1, CHOH), 7.42 (s, 1, COH), 7.8–9.0 (m, 8, CH_2), 9.05 (s, 3, CH_3), and 9.11 (s, 3, CH_3).

cis*-4,4-Dimethylbicyclo[4.1.0]heptan-2-ol** (cis*-5**) was synthesized by the procedure described by Dauben and Berezin,[9b] except that the zinc–copper couple was prepared by the method of LeGoff.[28] From 22 g (~0.34 g-atom) of zinc–copper couple, 0.1 g of iodine, 66 g (0.25 mol) of methylene iodide, and 12.6 g (equivalent to 0.093 mol) of **4** (from the previous preparation) in 140 ml of dry ether was obtained 9.9 g of product, bp 65° (1.5 mm), which was ~92% *cis*-**5** (71% yield). The impurities were [by nmr and gc (column SE30-1 at 100°)] 6% unchanged **4** and a trace of 3-iodomethyl-5,5-dimethylcyclohexene. A forefraction [bp 55–65° (1.5 mm)] which weighed 2.4 g and was 2/3 *cis*-**5** was also obtained; the total yield of *cis*-**5** was therefore 82%. Relative retention times on column SE30-1 at 100° were methylene iodide, 0.8; **4**, 1.0; *cis*-**5**, 2.5; 3-iodomethyl-5,5-dimethylcyclohexene, 6.2. Gc analysis (column TCEPE-1) of the main fraction showed that no (*i.e.* <0.5%) *trans*-**5** was present.

After gc purification (column SE30-2) *cis*-**5** exhibits the following spectral data: ir 3340, 3070, 3005, 1465, 1385, 1365, 1291, 1167, 1114, 1035, 983, 945, 919, 852, 807, and 743 cm^{-1}; nmr τ 5.76 (5 line m, 1, J_{21} = 6, J_{23} = 12, and $J_{23'}$ = 6 Hz, CHOH), 6.41 (s, 1, OH), 8.0–9.7 (m, 7, CH_2 and cyclopropyl), 9.10 (s, 3, CH_3), 9.17 (s, 3, CH_3), and 9.83 (t, 1, J = 5 Hz, cyclopropyl).

Anal. Calcd for $C_9H_{16}O$: C, 77.11; H, 11.49. Found: C, 76.99; H, 11.16.

6-Bromo-4,4-dimethylcycloheptene (**6**).—Five grams (0.03 mol) of 90% *cis*-**5** was stirred with 20 ml of 48% hydrogen bromide for 6 hr at room temperature, after which time the organic layer was separated and the aqueous layer extracted with pentane. The combined organic layers were shaken with aqueous sodium carbonate and then dried over anhydrous magnesium sulfate. The pentane was distilled and the residue distilled *in vacuo* to afford 6.7 g at 45–51° (1.0 mm). Analysis by nmr and gc (column SE30-2 at 100°) showed the distillate to be 93% **6** (95% yield), 5% *cis*-2-bromo-4,4-dimethylbicyclo[4.1.0]heptane (**7**),[10] and 1–2% 3-bromomethyl-5,5-dimethylcyclohexene (**8**).[10] A sample of **6** was obtained in ~97% purity by gc (column TCEP-1 at 60°; a small amount of isomerization to **8** occurred even under these mild conditions): ir 3025, 1705, 1645, 1385, 1370, 1315, 1173, 867, 788, 716, 679, and 630 cm^{-1}; nmr τ 4.3 (m, 2, C=CH), 6.9 (broad m, 1, CHBr), 7.28 (m, 2, C=CCH_2CBr), 7.5–8.5 (m, 4, C=CCH_2 and CH_2CBr), 9.02 (s, 3, CH_3), and 9.04 (s, 3, CH_3); mass spectrum m/e 202.025 [calcd for $C_9H_{15}Br(^{79}Br)$: 202.036; 202:204 intensity ratio = 0.9], 67 (base peak).

Anal. Calcd for $C_9H_{15}Br$: C, 53.19; H, 7.45. Found: C, 53.50; H, 7.46.

Dehydrobromination of 6-Bromo-4,4-dimethylcycloheptene (**6**).

A. With Quinoline.—A solution of 15 g (0.07 mol) of 93% **6** and 35 ml of distilled quinoline was heated at 195° for 20 min, cooled, and then added to enough dilute hydrochloric acid to produce an acidic solution. The hydrocarbon layer was separated and the aqueous layer extracted twice with pentane. After distillation of the pentane the residue was distilled *in vacuo* to afford a fraction, bp 60–70° (16 mm), which weighed 7.4 g (82% yield). analysis by gc (column CW20M-4 at 90°) showed the distillate to consist of at least five compounds, the relative amounts of which are given in Table I; analyses for 1 and 2 min reaction times in small-scale runs are given in Table II. The products were purified by using the above column and had the following relative retention times: **10**, 1.00; **11**, 1.25; **12**, 1.47; **13**, 1.59; **14**, 1.68. A mixture of these five isomers gave the following analysis.

Anal. Calcd for C_9H_{14}: C, 88.44; H, 11.56. Found: C, 88.28; H, 11.57.

1,5,5-Trimethyl-1,3-cyclohexadiene (**10**).—The uv spectrum of this isomer [λ_{max}^{hexane} 261 nm (ϵ 5400)] agrees with previously determined data[18] as does the mass spectrum [m/e 122.107 (calcd for C_9H_{14}: 122.109), 79 (base peak)]. The ir spectrum agrees with previously determined spectra[18] except that it shows additional small peaks at 1030, 997, and 818 cm^{-1} which are also present in the spectrum of 2,6,6-trimethyl-1,3-cyclohexadiene (**23**) and which we attribute to a ~15% impurity of the latter isomer. The nmr spectrum of pure **10**[18b] exhibits signals at τ 4.18–4.83 (complex m, 3, C=CH), 8.05 (narrow m, 2, C=C-CH_2), 8.25 (narrow m, 3, C=C-CH_3), and 8.87 (s, 6, CH_3).

5,5-Dimethyl-3-methylenecyclohexene (**11**).—The ir spectrum is in excellent agreement with previously determined spectra,[18] as are the uv spectrum [λ_{max}^{hexane} 231 nm (ϵ 19,900)] and mass spectrum [m/e 122.108 (calcd for C_9H_{14}: 122.109), 107 (base peak)]. The nmr spectrum[18b] exhibits signals at τ 3.88 (doublet of triplets, 1, J = 10 and 2 Hz, respectively, CH=C-CH_2), 4.33 (doublet of triplets, 1, J = 10 and 4 Hz, respectively, C=CH-CH_2), 5.23 (complex m, 2, C=CH_2), 7.95 (doublet of doublets, 2, J = 1.3 and 1.5 Hz, CH_2-C=CH_2), 8.08 (complex m, 2, J = 1.2 and and 4 Hz, CH_2CH=CH), and 9.09 (s, 6, CH_3); mass spectrum m/e 122.108 (calcd for C_9H_{14}: 122.109), 107 (base peak).

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6,6-Dimethyl-1,4-cycloheptadiene (**12**) shows only end absorption in the uv ($\epsilon_{210\,nm}^{hexane}$ 1700): ir 3035, 3010, 1650, 1375, 1365, 1133, 988, 812, 696, and 662 cm^{-1}; nmr τ 4.27 (m, 2, C=CH, 4.68 (s, 2, C=CH), 7.23 (broad s, 2, $(C{=}C)_2CH_2$), 7.80 (broad d, 2, J = 5 Hz, C=C-CH_2), and 8.98 (s, 6, CH_3); mass spectrum m/e 122.105 (calcd for C_9H_{14}: 122.109), 79 (base peak).

6,6-Dimethyl-1,3-cycloheptadiene (**13**) gave the following: λ_{max}^{hexane} 246 nm (ϵ 6160); ir 3060, 3020, 1615, 1385, 1370, 992, 789, 690, and 654 cm^{-1}; nmr τ 4.24 (broadened s, $W_{1/2}$ = 3.5 Hz, 4, C=CH), 7.93 (broadened d, 4, J = 3 Hz, $C{=}CCH_2$), and 9.03 (s, 6, CH_3); mass spectrum m/e 122.108 (calcd for C_9H_{14}: 122.109), 79 (base peak).

5,5-Dimethyl-1,3-cycloheptadiene (**14**) gave the following: λ_{max}^{hexane} 248 nm (ϵ 13,200); ir 3055, 3005, 1610, 1375, 1360, 1125, 976, 866, and 700 cm^{-1}; nmr τ 4.31 (apparent d, 2, line separation = 3.5 Hz, C=CH), 4.49 (apparent d, 2, line separation = 2.5 Hz, C=CH), 7.55–8.0 (m, 2, $C{=}CCH_2$), 8.45 (doublet of doublets, 2, J = 5 and 6.5 Hz, CH_2), and 8.96 (s, 6, CH_3); mass spectrum m/e 122.111 (calcd for C_9H_{14}: 122.109), 79 (base peak).

B. Dehydrobromination of 6 with Potassium Amide in Liquid Ammonia.—To a 5 mm × 10 cm Pyrex tube at ~ −78° was added ~0.2 ml of liquid ammonia and ~0.02 g of potassium metal. The tube was sealed, warmed to room temperature until formation of potassium amide was complete (color change from blue to gray), cooled, and opened. A solution (0.015 ml) of **6** and tridecane in a molar ratio of 2.2:1 was then added and the tube resealed and warmed to room temperature for 5 min (during which time a red color developed). The tube was then cooled and opened, and the solution quenched in water and extracted with pentane. Gc analysis (column CW20M-1 at 90°) showed a trace of unchanged **6** and three cycloheptadienes (see Table I) with a cycloheptadiene to tridecane ratio of 0.6:1 (27% recovery). an even lower recovery (~5%) was obtained when this reaction was run for 20 min at −33°.

C. Dehydrobromination of 6 with Potassium Hydroxide in Ethanol.—To a solution of 10 g of potassium hydroxide in 12 ml of absolute ethanol (in an argon atmosphere) was added 5.0 g (0.024 mol) of 98% pure **6** containing ~2% **8**. The reaction mixture was stirred at reflux for 0.5 hr, cooled, diluted with 30 ml of water, and extracted three times with pentane. The pentane solution was dried over anhydrous magnesium sulfate and distilled to afford 2.14 g (73% yield), which was shown by gc (column CW20M-1 at 90°) to contain 89% **13**, 8% **14**, and ~3% **10** and **11** (which probably arose from **8** present as an impurity). Less than 1% **6** remained, as shown by gc analysis on column SE30-1 at 90°.

Control Experiments. A.—Solutions of 5 μl of various dienes (along with tridecane as an internal standard) and 200 μl of quinoline or 0.1 M quinoline hydrobromide in quinoline were heated in a sealed tube under argon at 200° for 1 hr. The tubes were cooled and opened, and dilute hydrochloric acid was added until the quinoline had dissolved and the solution was acidic. The product mixtures were than extracted with 50 μl. of pentane and the pentane layers analyzed by gc (column CW20M-2 at 90°). When a mixture of 96% **11** and 4% **10** [which may have contained some 2,6,6-trimethyl-1,3-cyclohexadiene (**23**)] was heated in quinoline hydrobromide-quinoline at 200° for 1 hr the product mixture contained 33% **10** (+**23**), 49% **11**, 3% **12**, 8% **13**, and 7% **14**; no cycloheptadienes were formed when the initial mixture was heated for 1 hr at 200° in quinoline alone. Additional control experiments are given in Table IV.

TABLE IV
ISOMERIZATION OF CYCLOHEPTADIENES AT 200° FOR 1 HR

	Relative amount, %		
Isomer	Initial mixture	Final mixture (in quinoline)[a]	Final mixture (in 0.1 M quinoline hydrobromide in quinoline)[b]
10 + 11	<0.5	<0.5	<0.5
12	9	7	8
13	55	51	48
14	37	41	43

[a] 28% material loss. [b] 12% material loss.

B.—Solutions of 5 μl of cycloheptadienes (along with tridecane as an internal standard) in saturated potassium hydroxide–absolute ethanol were sealed in tubes under argon and immersed in refluxing saturated solutions of potassium hydroxide–ethanol (95°) for 30 min. The tubes were cooled and opened and dilute hydrochloric acid was added until the reaction mixtures became acidic. The contents of the tubes were then shaken with 50 μl of pentane and the pentane layers were analyzed by gc (column CW20M-2 at 90°). When a mixture of 97% **13** and 3% **14** was treated as above there was no change in the ratio of isomers. The results of additional experiments are given in Table V.

TABLE V
ISOMERIZATION OF CYCLOHEPTADIENES IN POTASSIUM HYDROXIDE–ETHANOL AT 95° FOR 30 MIN

	Relative amounts, %		
Isomer	Initial mixture[a]	Run 1 final mixture[a]	Run 2 final mixture[a,b]
12	24	0.6	0.6
13	43	58	62
14	32	41	38

[a] Average of two gc analyses. [b] There was <10% material loss.

6-Acetoxy-4,4-dimethylcycloheptene (**17**).—A solution of 1.0 ml of acetic acid, 3.3 ml of freshly distilled acetic anhydride, and 0.5 g (0.0032 mol) of ~90% *cis*-4,4-dimethylbicyclo[4.1.0]-heptan-2-ol (*cis*-**5**) was stirred at reflux for 26 hr, cooled, and carefully added to saturated aqueous sodium carbonate. The organic layer was separated and the aqueous layer extracted with pentane. The solvent was distilled from the combined organic layers and the residue flash distilled *in vacuo* to afford 0.4 g of product. Analysis by gc (column SE30-1 at 90°) showed this to be 92% **17** (63% yield) with ~4% each of two impurities, one of which had a retention time which corresponded to that of **16**.

After gc purification (column SE30-2 at 120°) **17** had ir 3030, 1735, 1645, 1365 (broad), 1240, 1020, 955, 863, 790, 695, and 680 cm^{-1}; nmr τ 4.26 (m, 2, C=CH), 5.27 (broad 7 line m, 1, J = 4.5, 4.5, 9, and 9 Hz, CHOAc), 7.55–8.55 (m, 6, CH_2), 8.07 (s, 3, $COCH_3$), and 9.01 (s, 6, CH_3).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 73.50; H, 9.97. Found: C, 73.20; H, 9.84.

In a peliminary experiment, a sample of *cis*-**5** [which contained 25% 3-iodomethyl-5,5-dimethylcyclohexene (**22**) and 10% 3,3-dimethylcyclohexanol (**21**)] was treated as above for 6 hr and worked up in a similar manner. Gc analysis of the crude reaction mixture (column CW20M-3 at 100°) showed a major component (65%), 19% **22** (by comparison of nmr spectra), 9% 3-acetoxy-1,1-dimethylcyclohexane, and several other peaks. The major component was isolated on the same column and was shown by nmr spectroscopy to be a 3:2 mixture of *cis*-2-acetoxy-4,4-dimethylbicyclo[4.1.0]heptane (**16**) and **17**: nmr τ 4.3 (broad m, 0.8, C=CH of **17**), 4.73 (5 line m, 0.6, J = 6.6 and 12 Hz, AcOCH of **16**), 5.3 (broad m, 0.4, AcOCH of **17**), 8.05 (s, 1.8, $COCH_3$ of **16**), 8.08 (1.2, $COCH_3$ of **17**), 7.6–9.6 (m), 8.99 (s, CH_3 of **16** and **17**), 9.14 (s, CH_3 of **16**), and 9.83 (t, 0.6, cyclopropyl H of **16**).

The component present as 9% of the mixture was purified by gc (column CW20M-3) and identified as 3-acetoxy-1,1-dimethylcyclohexane on the basis of spectral data: ir 1735, 1365 (broad), 1240, 1052, 1023, 980, 872, and 606 cm^{-1}; nmr τ 5.0–5.6 (m, 1, CHOAc), 8.06 (s, 3, OCH_3), 8.1–9.0 (m, 8, CH_2), and 9.05 (s, 6, CH_3).

Pyrolysis of 6-acetoxy-4,4-dimethylcycloheptene (**17**) was performed by passing 0.12 ml of **17** through a 12 cm × 1 cm Pyrex tube filled with glass helicies and heated to 516°. A flow rate of 30 ml/min of nitrogen was employed. Pentane was added to the pyrolysate and this mixture was washed with dilute sodium carbonate. The product (recovered in >50% yield) was shown by gc (column CW20M-2 at 90°) to consist of 11% **12** (by peak enhancement), 37% **13**, 37% **14** (both by comparison of ir spectra), and 15% of several unidentified compounds. No **17** remained and there was a maximum of 2% *m*-xylene present.

When an acetate sample which was predominantly a 3:2 mixture of **16** and **17** was pyrolyzed and worked up as above, the product mixture was shown by gc (column CW20M-4 at 90°) to consist of 38% *m*-xylene (by comparison of ir and nmr spectra), 11% **13** and **14** (by peak enhancement), and at least seven other components. At 506° there was ~30% unchanged starting

TABLE VI
PRODUCTS OF DEHYDRATION OF *cis*-4,4-DIMETHYLBICYCLO[4.1.0]HEPTAN-2-OL

Product	% of mixture Run 1	% of mixture Run 2	Relative retention time (column CW20M-2 at 90°)
18	45[a]	14	1.00
12	2	5	1.37
13	9	9	1.27
14	6	6	1.15

[a] Isolated along with 9% 11 (as determined by gc and nmr).

material, whereas at 528° there were no acetates and some charring was evident.

Dehydration of *cis*-4,4-dimethylbicyclo[4.1.0]heptan-2-ol (*cis*-5) was effected by heating 2.0 g (0.014 mol) of the alcohol with a few crystals of *p*-toluenesulfonic acid at ~230°. Products were slowly distilled from the reaction mixture (~1 g in 4.5 hr). In a second run a similar yield was produced in 0.5 hr by heating at 235° with a Wood's metal bath.

The product mixtures were analyzed by gc (column CW20M-2 at 90°; see Table VI) and several components were collected (column CW20M-4 at 90°). Cycloheptadienes **13** and **14** were identified by comparison of their ir spectra with those of authentic samples, **12** was tentatively identified by gc peak enhancement, and the major component in each run was identified as 4,4-dimethylbicyclo[4.1.0]hept-2-ene (**18**) on the basis of its nmr spectrum: τ 4.29 and 4.67 (AB quartet, 2, J = 10 Hz, CH=CH), 8.0–9.6 (m, 5, CH_2 and cyclopropyl H), 8.96 (s, 3, CH_3), 9.06 (s, 3, CH_3), and 9.72–10.02 (m, 1, cyclopropyl H).

Pyrolysis of 4,4-Dimethylbicyclo[4.1.0]hept-2-ene (18).—When the product mixture from dehydration run 1 was pyrolyzed, either in a sealed tube under argon at 320° for 5.5 hr, or in a flow system (described above) at 490°, analysis by gc (column CW-20M-2) and nmr showed that, in each case, about 50% of the product mixture was *m*-xylene.

Registry No.—**2**, 6267-39-6; **3**, 4694-17-1; **4**, 25866-56-2; *cis*-**5**, 25866-57-3; **6**, 25866-58-4; **10**, 25866-59-5; **11**, 25907-92-0; **12**, 25866-60-8; **13**, 25866-61-9; **14**, 25866-62-0; **16**, 25866-63-1; **17**, 25866-64-2; **18**, 25866-65-3; 3-acetoxy-1,1-dimethylcyclohexane, 25866-66-4.

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Hydroboration of Terpenes. VII. Hydroboration of (−)-Thujopsene. Configurations of the Isomeric 3-Thujopsanols and 3-Thujopsanones[1]

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Conformational analysis suggests that thujopsene (**1**) can exist in two possible conformations, steroidal I and nonsteroidal II. In the steroidal conformation, the side (α) away from the cyclopropane ring should be relatively inaccessible to reactions sensitive to steric requirements, whereas, in the nonsteroidal conformation, it is the side (β) toward the cyclopropane ring that should be relatively inaccessible. Hydroboration of (−)-thujopsene takes place exclusively from the β side, as indicated by the isolation of a single alcohol (+)-3-thujopsanol (**2**). The structure of (+)-3-thujopsanol has been established by determining the absolute configuration of the alcohol by Horeau's method. Similarly, epoxidation of thujopsene takes place predominantly from the β side to yield not the epoxide, but the rearranged product (−)-3-isothujopsanone (**5**). An equilibration study indicates nearly equal stability for (−)-3-thujopsanone and (−)-3-isothujopsanone. Consequently, it is concluded that thujopsene (**1**) reacts preferentially in the steroidal conformation I and probably exists preferentially in that conformation. In the course of this study all four of the isomeric 3-thujopsanols and both the two isomeric 3-thujopsanones were prepared and characterized.

The chemistry and structure of the sesquiterpene, thujopsene, has been the subject of considerable interest in the recent years. The structure of thujopsene was correctly deduced, in 1960, by Erdtman and Norin,[3] who assigned the relative stereochemistry shown in **1**. The cis relationship of the angular methyl substituent and the cyclopropane ring has subsequently been confirmed by a further degradative study[3d] and by a stereospecific synthesis.[4] Recently thujopsene has become of interest with respect to the problem of classical and nonclassical carbonium ion structures. Recognition of the existence of four rapidly equilibrating cyclopropyl carbinyl cations, from *cis*- and *trans*-thujopsenes, points to the essentially classical nature of these cations.[5]

Conformation and Steric Course of Reaction in Thujopsene.—Thujopsene is an interesting molecule, whose molecular model indicates the presence of considerable flexibility arising from the cis ring junction. The molecule (Figure 1) may adopt either the steroidal I or the nonsteroidal conformation II.[6] In the steroidal conformation I, the β side[7] provides a less crowded environment for the double bond. Hence the approach of any reagent with large steric requirements should be preferred from this side. On the other hand, in the nonsteroidal conformation II, the β side of the molecule is congested by the bridgehead 4a-methyl. However, the α side is relatively open to the reagent.

Hydroboration of olefins is highly sensitive to the steric environment of the double bond, taking place from the less hindered side.[8] The reaction is also highly exothermic but is remarkably free of skeletal rearrange-

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(1) Presented in part at the International Symposium on the Chemistry of Natural Products (IUPAC), London, July 1968.

(2) Postdoctoral Research Associate, 1966–1968, on Grant GM-10937 of the National Institutes of Health.

(3) (a) H. Erdtman and T. Norin, *Chem. Ind. (London)*, 622 (1960); (b) T. Norin, *Acta Chem. Scand.*, **15**, 1676 (1961); (c) S. Farsen and T. Norin, *ibid.*, **15**, 592 (1961); (d) T. Norin, *ibid.*, **17**, 738 (1963).

(4) (a) W. G. Dauben and A. C. Aschcraft, *J. Amer. Chem. Soc.*, **85**, 3673 (1963); (b) G. Büchi and J. D. White, *ibid.*, **86**, 2884 (1964).

(5) W. G. Dauben and L. E. Friedrich, *Tetrahedron Lett.*, **18**, 1735 (1967).

(6) For steroidal and nonsteroidal conformations, see C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, New York, N. Y., 1960, p 186 ff.

(7) It is convenient to use β to indicate the side of the molecule toward the cyclopropane ring and the bridgehead 4a-methyl, and α to indicate the other side of the molecule.

(8) (a) G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, **86**, 393 (1964); (b) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201 (1970).