tion was accomplished using polyphosphoric acid yielding, after distillation, 0.5 g (55% yield) of pure benzosuberene: bp 100° (10 mm); $n^{24}D$ 1.5863 [lit.[14] bp 100–102° (10 mm); $n^{25}D$ 1.5867]; nmr (CCl_4) δ 2.0 (m, 2 H), 2.35 (m, 2 H), 2.85 (m, 2 H), 5.8 (sextet, 1 H, J = 12.5 and 1.5 Hz, vinyl), 6.4 (sextet, 1 H, J = 12.5 and 1.5 Hz, vinyl), and 7.0 ppm (s, 4 H, aromatic); mass spectrum (70 eV) m/e (rel intensity) 144 (45), 129 (100), 128 (35), 116 (20), 115 (27).

Registry No.—**10**, 6571-72-8; **13**, 34825-86-0; **14**, 34825-87-1; **16**, 21564-79-4.

Acknowledgment.—The authors wish to thank the Academic Senate Committee on Research of the University of California, Davis, for partial support of this research.

Cyclopropylcarbinyl–Allylcarbinyl Radical Rearrangements in the Simple Bicyclo[3.1.0]hexyl and -[4.1.0]heptyl Systems

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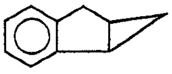
A study of the low-temperature photoinitiated free-radical tri-*n*-butyltin hydride reductions of the 2-bicyclo[3.1.0]hexyl and -[4.1.0]heptyl chlorides is reported. Cyclopropylcarbinyl–allylcarbinyl radical rearrangements in these systems were observed to be very selective, yielding almost entirely the primary allylcarbinyl radical products *via* external cyclopropane bond fission. Studies of the reversibility of the cyclopropylcarbinyl–allylcarbinyl radical rearrangements in the bicyclo[3.1.0]hexyl and -[4.1.0]heptyl systems, by means of tri-*n*-butyltin hydride reductions of the corresponding allylcarbinyl halides, were also carried out. Reversibility was observed, under the reduction conditions employed, only with the 3-cyclopentenylmethyl and 4-cycloheptenyl radicals.

In previous papers[1,2] we reported our studies, by means of both free-radical bromination and tin hydride reduction procedures, of cyclopropylcarbinyl–allylcarbinyl free-radical rearrangements in the cycloprop[2,3]indene (**1**) benzobicyclo[4.1.0]heptene (**2**) systems. It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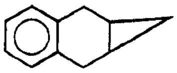
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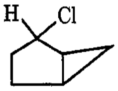
was noted that with both systems rearrangement of cyclopropylcarbinyl radicals to primary allylcarbinyl radicals proceeds in preference to rearrangement to secondary benzylic or simple secondary allylcarbinyl radicals, respectively. Based on the stabilities expected for the rearranged radical products,[3] the opposite behavior might have been predicted. However, a reasonable explanation is that the directionality of the rearrangements is controlled by overlap between the orbital containing the odd electron and the adjacent orbitals of the cyclopropane ring, leading to the primary radical being most favorable, and of more importance than the stabilities of the radical products as reflected in the energies of the respective activated complexes for rearrangement. This is similar to the stereoelectronic, conformational control argument proposed by Dauben[4] to explain the preferred direction of cyclopropylcarbinyl–allylcarbinyl rearrangements of the 2-hydroxybicyclo[3.1.0]hex-2-yl and -[4.1.0]hept-2-yl radicals.[5]

In order to examine in greater detail the apparent preference of cyclopropylcarbinyl radicals in bicyclo[*n*.1.0]alkyl systems to undergo external cyclopropane bond fission during rearrangement to give primary allylcarbinyl radicals rather than undergo internal bond fission to give secondary allylcarbinyl radicals, a study of cyclopropylcarbinyl radical rearrangements in the simple bicyclo[3.1.0]hexyl and -[4.1.0]heptyl systems was undertaken. To do this, the chlorides **3** and **4** were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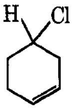
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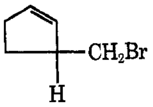

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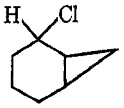
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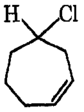
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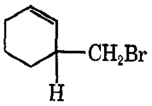

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reduced under free-radical conditions[6] using tri-*n*-butyltin hydride. In these systems any effects, either steric, electronic, or conformational, due to the phenyl substituents present in the analogous cycloprop[2,3]indene (**1**)[1] or benzobicyclo[4.1.0]heptene (**2**)[2] systems or to the α-hydroxy groups in Dauben's[4] compounds, are not present. To be able to better understand the results obtained with the cyclopropylcarbinyl systems, we also carried out tri-*n*-butyltin hydride reductions on the halides **5–8**, related to the allylcarbinyl radicals which might be produced by cyclopropylcarbinyl–allylcarbinyl rearrangements of the initial radicals produced from **3** and **4**. It was necessary to use the bromides rather than the chlorides in the primary systems **7** and **8** because of the low reactivities of the chlorides under our low-temperature tin hydride reduction conditions.

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[1] E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, **36**, 971 (1971).

[2] E. C. Friedrich and R. L. Holmstead, *ibid.*, **37**, 2546 (1972).

[3] (a) S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **90**, 2832 (1968); (b) D. C. Neckers, A. P. Schaap, and J. Hardy, *ibid.*, **88**, 1265 (1966); (c) D. C. Neckers and A. P. Schaap, *J. Org. Chem.*, **32**, 22 (1967).

[4] W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deving, *ibid.*, **34**, 2512 (1969).

[5] After the present work was already completed, a communication by A. L. J. Beckwith and G. Phillipou, *Chem. Commun.*, 658 (1971), appeared describing an elegant, clear-cut example in which highly selective stereoelectronic control of radical fragmentation in the 3β,5-cyclocholestan-6-yl radical takes place. Also, P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **36**, 905 (1971), reported that free-radical addition of methanethiol to bicyclo[3.1.0]hex-2-ene gives, selectively, besides the bicyclic product resulting from simple addition to the double bond, *cis*- and *trans*-3-methyl-5-thiomethylcyclopentene. No evidence for cyclopropane ring opening to form a secondary radical was observed.

[6] (a) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 229 (1968); (b) W. P. Neumann, "The Organic Chemistry of Tin," Wiley, New York, N. Y., 1970.

Results and Discussion

Synthesis of Starting Halides.—2-Chlorobicyclo[3.1.0]hexane (**3**) (89% endo, 11% exo) was prepared in 80% yield, as described by Freeman and coworkers,[7] by the reaction of thionyl chloride with *endo*-2-bicyclo[3.1.0]hexanol. 2-Chlorobicyclo[4.1.0]heptane (**4**) (82% endo, 18% exo) in 90% yield and 4-chlorocyclohexene(**5**) in 90% yield were prepared by similar procedures starting with *endo*-2-bicyclo[4.1.0]heptanol and 4-hydroxycyclohexene, respectively.

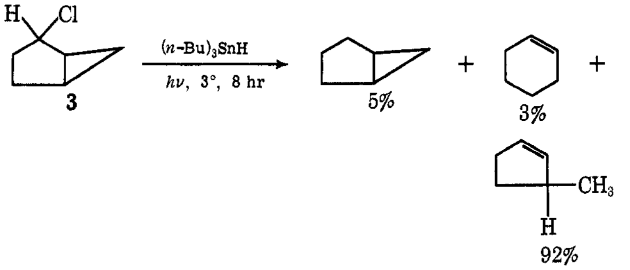
Attempts to prepare a pure sample of 4-chlorocycloheptene (**6**) by reaction of 4-hydroxycycloheptene with thionyl chloride and tri-*n*-butylamine in ether under reflux, or by reaction of *endo*-2-bicyclo[4.1.0]heptanol with 37% hydrochloric acid at room temperature, were unsuccessful. In the first case a 43% yield of a 70:30 mixture, and in the second case a 90% yield of a 82:18 mixture, of **6** and 3-(chloromethyl)cyclohexene was obtained. Attempts to separate the isomeric chlorides by preparative glpc were not successful. However, a technique was devised for carrying out the organotin hydride reductions directly on the mixture so that separation of the isomeric chlorides was not absolutely necessary.

In the preparation of 3-(bromomethyl)cyclopentene (**7**), the procedure of Hanack and Schneider[8] was employed with only slight modifications for the synthesis of methyl cyclopentene-3-carboxylate. The methyl ester was then reduced to 3-(hydroxymethyl)cyclopentene in 81% yield using the selective Vitride reagent.[9] Reaction of the alcohol with triphenylphosphine and carbon tetrabromide in dichloromethane[10] gave, after work-up and distillation, a mixture consisting of 40% bromoform and 60% **7** (55% yield). The bromide **7** was purified by preparative scale glpc.

For the preparation of 3-(bromomethyl)cyclohexene (**8**) advantage was taken of a side reaction reported by Staley and Wiseman[11] in their studies of the reaction of 5,5-dimethylcyclohexen-3-ol with methylene iodide and a zinc–copper couple. Thus, 3-hydroxycyclohexene upon reaction with methylene iodide and a zinc–copper couple under reflux in ether for 12 hr gave a 23% yield, after work-up and distillation, of pure 3-(iodomethyl)-cyclohexene.[12] This was then treated with tetraethylammonium bromide in DMF to give an 85% yield of **8**, based on starting iodide.

Tri-*n*-butyltin Hydride Reductions in the 2-Bicyclo[3.1.0]hexyl and Related Allylcarbinyl Systems.—All reductions described below were carried out at least in duplicate, and the product compositions reported are reproducible to ±2%. The tri-*n*-butyltin hydride to halide mole ratio was 1:1, and the yield of hydrocarbon products was greater than 97% in all cases. Also, controls showed that all reactants and products were stable toward rearrangement or further reaction, respectively, under the reduction conditions.

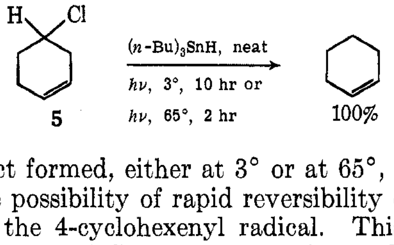
The 11% *exo*-, 89% *endo*-2-chlorobicyclo[3.1.0]hexane mixture (**3**) was reduced in the absence of a solvent with tri-*n*-butyltin hydride at 3° using light initiation. The results of the reductions are shown below.



3-Methylcyclopentene, the product obtained from rearrangement of the initially formed cyclopropylcarbinyl radical to give the primary allylcarbinyl radical, is formed in considerably higher yield than is cyclohexene. Thus, the direction of cyclopropylcarbinyl–allylcarbinyl radical rearrangement observed here is very similar to that observed in the cycloprop[2,3]indene system.[2]

The high selectivity of the ring fission in the reduction of **3** can be accounted for on the basis of better orbital overlap between the outer cyclopropane bond and the adjacent radical center, as Dauben[4] has suggested. From examination of molecular models it appears that maximum orbital overlap for opening of the outside cyclopropane bond requires a chair form conformation of the bicyclo[3.1.0]hexane ring. However, nmr studies[13] indicate that the preferred conformation of this system is a boat form. If this is the case, models suggest that orbital overlap control only slightly prefers fission of the outside over the inside bond of the cyclopropane ring. However, a planar five-membered ring also shows clear preference for opening of the outer bond.

It should be noted that selective formation of 3-methylcyclopentene could also result if the primary radical precursor of 3-methylcyclopentene is much more reactive toward hydrogen atom abstraction from the tin hydride than is the secondary radical precursor of cyclohexene, and if the secondary radical formation is rapidly reversible. To evaluate this possibility we carried out a tri-*n*-butyltin hydride reduction on 4-chlorocyclohexene (**5**) to find out whether any bicyclo[3.1.0]hexane or 3-methylcyclopentene, formed *via* ring closure to the cyclopropylcarbinyl radical, is obtained. The results are shown below. Cyclohexene was the sole product formed, either at 3° or at 65°, thus eliminating the possibility of rapid reversibility of the formation of the 4-cyclohexenyl radical. This result is similar to that of Slaugh,[14] who observed that the thermal decomposition of *tert*-butyl cyclohexene-4-percarboxylate at 140° in the presence of *p*-cymene gives cyclohexene as the only monomeric product. Thus, the orbital overlap explanation for selective



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[7] P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, **32**, 24 (1967).

[8] M. Hanack and H. J. Schneider, *Tetrahedron*, **20**, 1863 (1964).

[9] Hanack and Schneider[8] reported obtaining only a very small yield of the desired alcohol by reduction with lithium aluminum hydride.

[10] R. G. Weiss and E. I. Snyder, *J. Org. Chem.*, **36**, 403 (1971).

[11] S. W. Staley and F. L. Wiseman, Jr., *ibid.*, **35**, 3868 (1970).

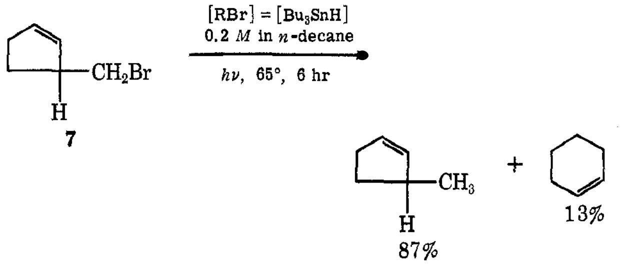
[12] Note that reaction of 3-hydroxycyclopentene with CH_2I_2 and a Zn-Cu couple under reflux in ether for 24 hr gave only a 28% yield of *endo*-2-bicyclo[3.1.0]hexanol and no observable 3-(iodomethyl)cyclopentene.

[13] S. Winstein, E. C. Friedrich, R. Baker, and Yang-I Lin, *Tetrahedron, Suppl. 8, Part II*, 621 (1966).

[14] L. H. Slaugh, *J. Amer. Chem. Soc.*, **87**, 1522 (1965).

fission of the outer bond of the cyclopropane ring in the bicyclo[3.1.0]hexane system seems to best explain the results obtained.

As a final experiment in our studies of cyclopropylcarbinyl–allylcarbinyl radical rearrangements and their reversibility in the bicyclo[3.1.0]hexane system, we carried out the tri-*n*-butyltin hydride reduction of 3-(bromomethyl)cyclopentene (**7**). Using a 1:1 mole ratio of **7** to tin hydride at 3° with light initiation in the absence of a solvent, only 3-methylcyclopentene was obtained. In an attempt to give the initially formed 3-cyclopentenylmethyl radical more time to undergo possible ring closure before capture by hydride occurred, we also carried out a reduction of **7** in *n*-decane solvent and at higher temperature. The results are shown below. The presence of cyclohexene in the product mixture indicates that ring closure to the cyclopropylcarbinyl radical, although slow, does actually occur. These results also agree with those of Slaugh,[14] who observed that the thermal decomposition of *tert*-butyl cyclopenten-3-yl-peracetate at 140° in the presence of *p*-cymene gives both 3-methylcyclopentene (12%) and cyclohexene (47%).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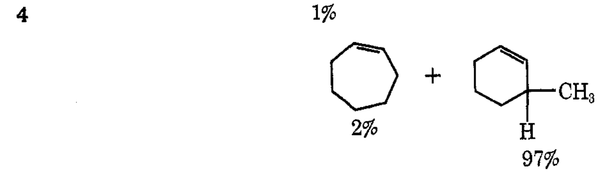
Tri-*n*-butyltin Hydride Reductions in the 2-Bicyclo[4.1.0]heptyl and Related Allylcarbinyl Systems.

—All reductions described in this section were also carried out at least in duplicate, and the product compositions reported are reproducible to ±2%. The yields of hydrocarbon products were greater than 97% in all cases. Controls showed that all reactants and products were stable toward rearrangement or further reaction, respectively, under the reduction conditions employed. All reductions were done using a 1:1 mole ratio of tri-*n*-butyltin hydride to halide.

The 18% *exo*-, 82% *endo*-2-chlorobicyclo[4.1.0]heptane mixture (**4**) was reduced at 3° using light initiation with tri-*n*-butyltin hydride in the absence of a solvent. The results shown below indicate that cyclopropylcarbinyl–allylcarbinyl radical rearrangement occurs here, as in the 2-bicyclo[3.1.0]hexyl system, with high selectivity to give a primary allylcarbinyl radical in preference to a secondary allylcarbinyl radical. Consideration of molecular models of the bicyclo[4.1.0]heptane system indicate that only when the cyclohexane ring is in the boat form is inside cyclopropane bond fission preferred. All other conformations would lead to better overlap of the p orbital containing the radical electron with the outside bond of the cyclopropane ring. Since a boat form bicyclo[4.1.0]heptane conformation is clearly unfavorable,[4] a similar orbital overlap argument to that advanced for the bicyclo[3.1.0]hexane system can be given to explain the very selective β scission of the outer cyclopropane bond in the present case.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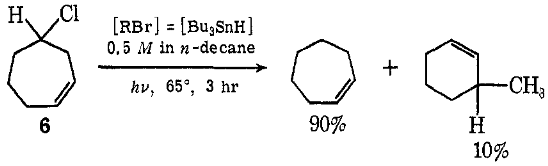
To examine the possibility of rapid reversibility of the 2-bicyclo[4.1.0]hexyl–cyclohepten-4-yl radical rearrangement, tri-*n*-butyltin hydride reduction of 4-chlorocycloheptene (**6**) was carried out. Unfortunately, as mentioned earlier, we were unable to obtain a pure sample of **6**, but only an isomeric mixture of **6** and 3-(chloromethyl)cyclohexene. However, the tin hydride reduction could still be carried out on this mixture, since control experiments showed a pure sample of 3-(chloromethyl)cyclohexene to be unreactive toward tri-*n*-butyltin hydride both at 3° and at 65° under the reaction conditions employed. Thus, the reduction of **6** with tri-*n*-butyltin hydride at 3° in the absence of a solvent gave cycloheptene as the only product. However, when the reduction was carried out at 65° and the reactants were diluted with *n*-decane, 3-methylcyclohexene was also formed. Thus, the cyclopropylcarbinyl–allylcarbinyl radical rearrangement in question is clearly reversible, although slow.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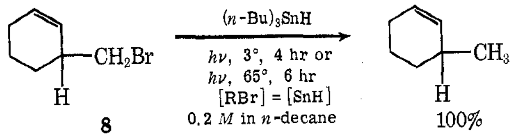
The last compound of the series to be studied was 3-(bromomethyl)cyclohexene (**8**). The reduction of **8** with tri-*n*-butyltin hydride both at 3° in the absence of a solvent, or at 65° in the presence of solvent *n*-decane, gave only 3-methylcyclohexene. Thus, reversibility of the 2-bicyclo[4.1.0]hexyl–cyclohexene-3-methyl radical rearrangement does not occur with either the low-temperature neat or high-temperature dilution conditions.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As a final point, brief comment should be made on the reasons for the observed reversibility or irreversibility of the cyclopropylcarbinyl–allylcarbinyl radical rearrangements studied in the present work. For example, allylcarbinyl–cyclopropylcarbinyl radical ring closure was observed indirectly with the 3-cyclopentenylmethyl and 4-cycloheptenyl radical systems, but was not observed at all with the 3-cyclohexenylmethyl and 4-cyclohexenyl radical systems under the reaction conditions employed. However, note that ring closure was clearly observed with both of the related indene-1-methyl[1] and 1,2-dihydronaphthalene-2-methyl[2] radical systems.

The simplest explanation for the occurrence or nonoccurrence of ring closure by an allylcarbinyl radical system is one based on orbital overlap considerations. For ring closure to be favorable the p orbital containing the odd electron and the orbitals of the double bond must be close enough together and of proper orientation for good overlap to take place. From inspection of simple molecular models it appears that the above conditions are better satisfied in the systems where ring closure was observed than in those systems where no ring closure took place, although the situation is not clear cut. The reason for the occurrence of ring closure with the 1,2-dihydronaphthalene-2-methyl radical[2] but not with the closely related simple 3-cyclohexenylmethyl radical is probably due mainly to flattening of the six-membered ring by the phenyl substituent in the former system, thus orienting the double-bond orbitals better for overlap with the radical center.

Experimental Section

Boiling points, nmr and mass spectra, and microanalyses were obtained as previously reported.[2]

Glpc Analyses.—These were done using a Varian Aerograph Series 1400 flame ionization instrument. Separation of the hydrocarbon products was carried out on a 3 m × 0.125 in. copper column with a 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on 60/80 mesh firebrick packing. The column temperature was maintained at 65° while the helium flow rate was 10–15 ml/min. The retention times in minutes of the various compounds encountered were, 3-methylcyclopentene, 2.2; bicyclo[3.1.0]hexane, 3.2; cyclohexene, 3.5; 3-methylcyclohexene, 5.8; bicyclo[4.1.0]heptane, 8.5; and cycloheptene, 8.7.

2-Chlorobicyclo[3.1.0]hexane (3).—The procedure used for the preparation of this material followed that of Freeman and coworkers.[7] 2-Chlorobicyclo[3.1.0]hexane was obtained in an 80% yield based on reacted *endo*-2-bicyclo[3.1.0]hexanol:[15] bp 50–70° (11 mm) (pot); n^{24}D 1.4912 (literature, no physical constants reported); nmr (neat) δ 0.5 (m, 2 H), 1.65 (b m, 6 H), and 4.5 ppm (m, 1 H, CHCl); mass spectrum (70 eV) *m/e* (rel intensity) 118 (3.08), 116 (9.67), 81 (44), 80 (100), 79 (48). The ratio of endo to exo chloride (89:11) formed was similar to that reported by Freeman.[7]

4-Chlorocyclohexene (5).—4-Hydroxycyclohexene, the precursor to **5**, was prepared by the method of Zelinski and Zitova.[16] Using the procedure of Zweifel, *et al.*,[17] for conversion of alcohols to the corresponding chlorides, 4-chlorocyclohexene was obtained from 4-hydroxycyclohexene in 90% yield: bp 35° (14 mm); n^{24}D 1.4813 (no literature[7] physical constants, only nmr spectrum reported); nmr (neat) δ 1.8 (b m, 6 H), 3.8 (m, 1 H, CHCl), and 5.3 ppm (b s, 2 H, vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 118 (3.08) 116 (9.67), 80 (100), 79 (48), 54 (42).

3-(Hydroxymethyl)cyclopentene.—Methyl cyclopentene-3-carboxylate, the precursor to 3-(hydroxymethyl)cyclopentene, was prepared *via* the method of Hanack and Schneider.[8] For the reduction of the methyl ester to the corresponding alcohol, the following procedure was used. To a 50-ml three-necked microware flask fitted with a calcium chloride drying tube, dropping funnel, and a low-temperature alcohol thermometer was added 3.0 g (24 mmol) of methyl cyclopentene-3-carboxylate and 30 ml of anhydrous ether. The magnetically stirred solution was then cooled to −40°, and 7.25 ml (7.5 g, 26 mmol of hydride) of Vitride reducing agent, diluted with 5 ml of anhydrous ether, was added dropwise over a period of 20 min. The resulting light yellow solution was stirred at −40° for 15 min longer, after which time the solution was allowed to warm up to 0°. At this point several drops of 20% sulfuric acid were added to destroy excess hydride. The resulting mixture was extracted twice with 20% sulfuric acid, water, and saturated sodium chloride solution and then dried over anhydrous magnesium sulfate. Removal of the ether yielded a light yellow liquid which upon distillation through a short-path apparatus gave 1.9 g (81% yield) of 3-(hydroxymethyl)cyclopentene: bp 52° (12 mm); n^{24}D 1.4745 [lit.[8] bp 51–53° (12 mm)]; nmr (CCl$_4$) δ 1.3–2.6 (b m, 4 H), 2.75 (m, 1 H, CHCH$_2$OH), 3.4 (d, 2 H, CH$_2$OH, J = 6.5 Hz), 4.85 (s, 1 H, OH), and 5.7 ppm (m, 2 H, vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 98 (1.31), 80 (18.8), 67 (100), 66 (14.5), 41 (28), 39 (23), 27 (10).

3-(Bromomethyl)cyclopentene (7).—The alcohol-bromide conversion procedure of Weiss and Snyder[10] was employed for the conversion of 3-(hydroxymethyl)cyclopentene to **7**. Bromoform, a side product of the reaction, was removed from the distilled reaction mixture by preparative glpc using a 2 m × 0.375 in. column packed with 10% silicone SF-96, 0.25% Carbowax 20M on 60/80 mesh Chromosorb G. Pure 3-(bromomethyl)cyclopentene was obtained in a 55% yield based on reacted 3-(hydroxymethyl)cyclopentene: bp *ca.* 53° (12 mm); n^{24}D 1.5066; nmr (CCl$_4$) δ 1.4–2.4 (b m, 2 H), 2.2–2.6 (m, 2 H), 3.0–3.5 (m, 1 H, CHCH$_2$Br), 3.3 (m, 2 H, CH$_2$Br), and 5.6–6.0 ppm (m, 2 H, vinyl); mass spectrum (70 ev) *m/e* (rel intensity) 162 (4), 160 (4.1), 81 (31), 79 (12), 67 (100), 53 (10), 41 (16), 39 (17), 27 (14).

Anal. Calcd for C$_6$H$_9$Br: C, 44.75; H, 5.63; Br, 49.62. Found: C, 44.61; H, 5.70; Br, 49.44.

2-Chlorobicyclo[4.1.0]heptane (4).—The procedure used was similar to that employed for the preparation of 2-chlorobicyclo[3.1.0]hexane.[7] 2-Chlorobicyclo[4.1.0]heptane was obtained in a 90% yield based on reacted *endo*-2-bicyclo[4.1.0]heptanol:[15] bp (pot) 50–70° (10 mm); n^{24}D 1.4921; nmr (neat) δ 0.05–0.34 (q, 0.36, exo CH$_2$ cyclopropyl, J = 5 Hz), 0.37–1.1 (complex multiplet, 1.64 H, endo CH$_2$ cyclopropyl), 1.6 (b m, 8 H), and 4.65 ppm (b m, 1 H, CHCl); mass spectrum (70 eV) *m/e* (rel intensity) 132 (3.27), 130 (9.97), 95 (71.9), 94 (31.7), 81 (57), 79 (100), 77 (25), 67 (49.5), 53 (37), 41 (51), 39 (79), 27 (56).

Anal. Calcd for C$_7$H$_{11}$Cl: C, 64.36; H, 8.48; Cl, 27.14. Found: C, 64.75; H, 8.61; Cl, 27.18.

The ratio of endo to exo bicyclic chlorides was determined to be approximately 82:18, as calculated by comparison of the nmr absorption values of the cyclopropylmethylene protons in *endo*- and *exo*-2-bicyclo[4.1.0]heptanol[18] to the values obtained for the bicyclic chloride mixture. The amount of exo chloride was thus determined from the quartet at 0.05–0.34 ppm, while the amount of endo chloride was determined from the multiplet at 0.37–1.1 ppm.

4-Hydroxycycloheptene.—The procedure used for preparation of this material was that of Friedrich and Winstein.[19] *endo*-2-Bicyclo[4.1.0]heptanol[15] (4.0 g, 35.7 mmol) was treated with 40 ml of a 0.5% by weight solution of 70% perchloric acid in glacial acetic acid at 50° for 45 min. The work-up consisted of extracting the resulting yellow solution with pentane, washing the pentane with three 25-ml portions of water, 20 ml of saturated NaHCO$_3$, and two 20 ml portions of saturated NaCl and drying the pentane extract over anhydrous MgSO$_4$. After removal of the pentane by distillation, the remaining liquid was added dropwise to a mixture of 1.35 g (35.7 mmol) of lithium aluminum hydride in 150 ml of anhydrous ether. This mixture was stirred at room temperature for 2 hr. The mixture was worked up in the usual manner, and after removal of the ether the resulting yellow liquid was distilled in a one-piece micro apparatus to give 3.4 g (85% yield) of pure 4-hydroxycycloheptene: bp (pot temperature) 80° (10 mm); n^{25}D 1.4869 [lit.[19] bp (pot temperature) 90° (20 mm); n^{25}D 1.4870]; nmr (CCl$_4$) δ 1.0–2.5 (b m, 8 H), 3.4 (m, 1 H, CHOH), 3.8 (s, 1 H, OH), and 5.6 ppm (m, 2 H, vinyl).

Attempted Preparation of Pure 4-Chlorocycloheptene (6).—Two procedures were tried. The first was similar to that reported earlier in the conversion of 4-hydroxycyclohexene to 4-chlorocyclohexene, but using 4-hydroxycycloheptene (3.0 g, 26.8 mmol). After the usual work-up procedure a dark liquid resulted which, upon distillation, yielded 1.5 g (43%) of a colorless liquid, bp *ca.* 65° (25 mm). Analysis of this liquid by nmr showed it to be a mixture of 4-chlorocycloheptene and 3-(chloromethyl)cyclohexene in a ratio of 70:30. Since 3-(chloromethyl)cyclohexene had already been prepared by an alternative route, described in a later section, its nmr spectrum was available. The nmr spectrum of 4-chlorocycloheptene was thus able to be determined by difference and is as follows: nmr (neat) δ 1.0–2.5 (b m, 6 H), 2.6 (t, 2 H, J = 6 Hz), 3.85 (m, 1 H, CHCl), and

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[18] K. E. Rubenstein, Ph D. Thesis, University of Wisconsin, 1967, pp 90, 94.

[19] E. C. Friedrich and S. Winstein, unpublished work.

5.7 ppm (m, 2 H, vinyl, J = 5.5 Hz). Quantitative values were determined using the vinyl region as an internal standard, the multiplet at 3.85 ppm of 4-chlorocycloheptene, and the sharp doublet at 3.38 ppm of 3-(chloromethyl)cyclohexene. Attempts to separate the isomeric mixture by preparative glpc using columns containing TCEP, NMPN, SE-30, and Carbowax 20M were not successful. Elemental analysis was thus carried out directly on the isomeric mixture.

Anal. Calcd for $C_7H_{11}Cl$: C, 64.36; H, 8.48; Cl, 27.14. Found: C, 64.61; H, 8.54; Cl, 26.94.

The other method attempted for the preparation of 6 was a modification of the procedure used by Staley and Wiseman[11] for the preparation of 4-bromo-6,6-dimethylcycloheptene. Into a small flask was placed 1 g (8.93 mmol) of *endo*-2-bicyclo[4.1.0]-heptanol[15] and 6 ml of 37% hydrochloric acid. This mixture was stirred at room temperature for 3 hr, after which time the solution was extracted with pentane. The pentane extract was washed with water, saturated sodium bicarbonate, and saturated sodium chloride, and dried over anhydrous sodium sulfate. Removal of the pentane yielded a light yellow liquid which upon distillation gave 1.05 g (90%) of an isomeric mixture of 4-chlorocycloheptene and 3-(chloromethyl)cyclohexene in a ratio of 82:18, respectively.

3-(Iodomethyl)cyclohexene.—The procedure used was a modification of that employed by Staley and Wiseman[11] for the preparation of 5,5-dimethyl-3-(iodomethyl)cyclohexene. The reaction of 30 g (0.31 mol) of 3-hydroxycyclohexene, 38 g (0.57 mol) of 30 mesh zinc-copper couple, and 110 g (0.41 mol) of methylene iodide in ether was carried out under reflux for 12 hr. At this point, the flask was cooled in an ice bath and then *ca.* 100 ml of saturated NH_4Cl was added slowly dropwise to the pink viscous mixture. Work-up was carried out in the usual manner. After removal of the ether by distillation, the remaining brownish liquid was distilled quickly through a small distillation apparatus to remove any starting material. The resulting distillate was then redistilled through a 60-cm spinning-band column to give 15.2 g (22.5%) of pure 3-(iodomethyl)cyclohexene: bp 85° (10 mm); $n^{24}D$ 1.5610; nmr (CCl_4) δ 1.7 (b m, 6 H), 2.35 (m, 1 H, $CHCH_2I$), 3.1 (d, 2 H, CH_2I, J = 7 Hz), and 5.7 ppm (m, 2 H, vinyl); mass spectrum (70 eV) m/e (rel intensity) 222 (0.44), 127 (8.44), 95 (100), 79 (9.9), 67 (22.5), 55 (15), 41 (26), 39 (21).

Anal. Calcd for $C_7H_{11}I$: C, 37.86; H, 4.99; I, 57.14. Found: C, 38.04; H, 5.05; I, 56.90.

3-(Chloromethyl)cyclohexene.—This material was prepared from 3-(iodomethyl)cyclohexene using a procedure similar to that employed by Weaver and Hutchinson[20] for the conversion of n-butyl iodide to n-butyl chloride. 3-(Iodomethyl)cyclohexene (3.0 g, 13.5 mmol) was added to a magnetically stirred solution of 1 g (23.5 mmol) of dry lithium chloride in 11 ml of anhydrous dimethylformamide (DMF). The reaction mixture was then heated at 50° for 48 hr. Work-up consisted of pouring the mixture into 20 g of ice and extracting the aqueous layer with three 20-ml portions of ether. The combined ether layers were washed several times with saturated NaCl and then dried over anhydrous $MgSO_4$. Removal of the ether gave a yellowish liquid which, when distilled, gave 1.5 g (85%) of 3-(chloromethyl)-cyclohexene: bp *ca.* 45° (10 mm); $n^{24}D$ 1.4832; nmr (CCl_4) δ 1.8 (b m, 6 H), 2.45 (m, 1 H, $CHCH_2Cl$), 3.38 (d, 2 H, CH_2Cl, J = 6.5 Hz), and 5.7 ppm (m, 2 H, vinyl); mass spectrum (70 eV) m/e (rel intensity) 132 (2.62), 130 (8.12), 95 (5.88), 81 (100), 53 (14.8), 41 (16.9), 27 (16.8).

Anal. Calcd for $C_7H_{11}Cl$: C, 64.36; H, 8.48; Cl, 27.14. Found: C, 64.53; H, 8.60; Cl, 27.27.

3-(Bromomethyl)cyclohexene (8).—Into a 50-ml erlenmeyer flask was placed 25 ml of anhydrous DMF, 4.78 g (20 mmol) of tetraethylammonium bromide, and 3.0 g (13.5 mmol) of 3-(iodomethyl)cyclohexene. The flask was then heated at 40° for 22 hr. The mixture was worked up in the same manner as described for the preparation of 3-(chloromethyl)cyclohexene. Distillation afforded 2.0 g (85%) of 3-(bromomethyl)cyclohexene: bp *ca.* 65° (10 mm); $n^{24}D$ 1.5128; nmr (CCl_4) δ 1.7 (b m, 6 H), 2.45 (m, 1 H, $CHCH_2Br$), 3.28 (d, 2 H, CH_2Br, J = 7 Hz), and 5.7 ppm (m, 2 H, vinyl); mass spectrum (70 eV) m/e (rel intensity) 176 (1.18), 174 (1.22), 95 (100), 81 (33.3), 67 (19.4), 53 (14.8), 41 (21.5), 39 (23.3).

Anal. Calcd for $C_7H_{11}Br$: C, 48.02; H, 6.33; Br, 45.54. Found: C, 48.33; H, 6.48; Br, 45.34.

Tri-n-Butyltin Hydride Reductions.—The free-radical tri-n-butyltin hydride reductions of the halides **3-8** were carried out following procedures similar to those described earlier.[1,2] Controls for reactant and product stabilities were in each case carried out under the reduction conditions in the presence of tri-n-butyltin halide. Hydrocarbon product characterization was accomplished by comparison of their nmr spectra and glpc retention times with those of known samples which were available in our laboratories. Qualitative results for yields of the hydrocarbon products were obtained by analytical glpc techniques, using conditions as described at the beginning of this Experimental Section.

Registry No.—**3,** 34825-89-3; **4,** 34825-90-6; **5,** 930-65-4; **6,** 32446-16-5; **7,** 17645-61-3; **8,** 34825-93-9; 3-(iodomethyl)cyclohexene, 34825-94-0; 3-(chloromethyl)cyclohexene, 19509-49-0.

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