Cyclopropylcarbinyl–Allylcarbinyl Radical Rearrangements in the Benzobicyclo[4.1.0]heptene System

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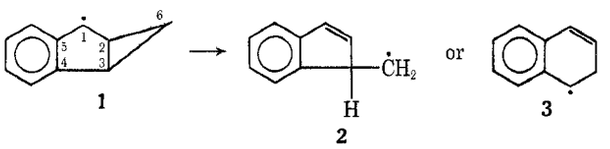
Received November 30, 1971

Preparation of benzobicyclo[4.1.0]hept-3-ene, and a study of its light-initiated free-radical bromination using *N*-bromosuccinimide in carbon tetrachloride, is reported. Also, an investigation of the free-radical tri-*n*-butyltin hydride reduction of 2-bromomethyl-1,2-dihydronaphthalene was carried out. In both the bromination and tin hydride reduction studies in the benzobicyclo[4.1.0]heptenyl system, examination of the product compositions revealed that the benzobicyclo[4.1.0]hepten-2-yl radical undergoes cyclopropylcarbinyl–allylcarbinyl rearrangement *via* 1,7 bond cleavage to the primary allylcarbinyl radical species in preference to rearrangement *via* 1,6 bond cleavage to the corresponding secondary allylcarbinyl radical species. This is explained as resulting mainly from orbital overlap control of the directionality of rearrangement.

In our earlier work on the azobisisobutyronitrile-initiated free-radical α bromination of cycloprop[2,3]-indene with *N*-bromosuccinimide (NBS) at 77° in carbon tetrachloride,[1,2] which proceeds *via* initial formation of the cyclopropylcarbinyl radical **1**, we found that the rearranged homoallylic bromide product derived from the primary homoallyl radical **2** was obtained in five times as great a yield as that obtained from the secondary benzylic homoallyl radical **3**. Also,



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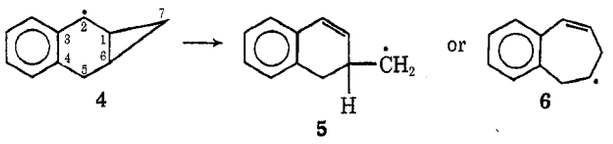
we later observed[2] that the organotin hydride reductions of 1-bromocycloprop[2,3]indene at low temperature gave 10–20% as much of the product resulting, after free-radical cyclopropylcarbinyl–allylcarbinyl rearrangement, from the primary radical **2** as from the benzylic radical **3**. Thus, it appears from both the bromination and organotin hydride reduction studies that on cyclopropylcarbinyl–allylcarbinyl radical rearrangement the cycloprop[2,3]inden-1-yl radical (**1**) prefers to undergo 2,6 bond cleavage to give a primary radical product rather than undergo 2,3 bond cleavage to give a benzylic radical product.

This result was somewhat unexpected. It is well known from other studies of free-radical reactions that, for electronic reasons, benzylic radicals are considerably more stable than primary radicals.[3] Thus, if these factors are reflected in the energies of the activated complexes for rearrangement of **1** to **2** or **3**, one might have expected to find much more rearrangement to the benzylic radical product **3**.

A possible explanation for the observation that rearrangement proceeds preferentially to the primary radical **2** may be that the phenyl group at the 3 position of the partially formed cycloprop[2,3]inden-1-yl radical (**1**) at the transition state for cyclopropylcarbinyl–allylcarbinyl radical rearrangement exhibits an electron-withdrawing inductive effect rather than an electron-releasing resonance effect. Thus, the 3 position would be destabilized to formation of the benzylic radical **3**, occurring *via* ring scission between carbons 2 and 3. An alternative explanation, however, could be that conformational control of the directionality of bond cleavage by more favorable orbital overlap between the p orbital at carbon 1 and the C_2–C_6 bond, as proposed by Dauben[4] to explain the direction of cyclopropylcarbinyl–allylcarbinyl rearrangement of the 2-hydroxybicyclo[3.1.0]hex-2-yl radical, is more important than electronic control and thus determines the course of the rearrangement.

One way to test the first explanation is to study cyclopropylcarbinyl–allylcarbinyl radical rearrangements in the structurally similar benzocyclo[4.1.0]hepten-2-yl[5] radical system **4**. In this system the 6 position of the



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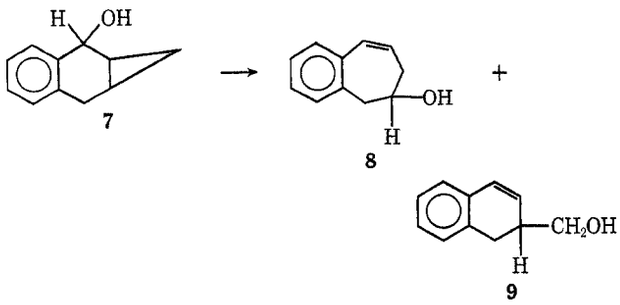
cyclopropane ring is insulated from the phenyl ring by a methylene group, and thus an inductive effect of the phenyl group should have little or no effect on 1,6 bond breaking to give the secondary benzocycloheptadienyl radical (**6**) *vs.* the primary radical **5**.

In connection with the above, it should be noted that, in work carried out by Julia and coworkers[6] on cationic cyclopropylcarbinyl reactions in the benzobicyclo-[4.1.0]heptene-2-yl system **7**, the product resulting formally from the cation related to **6** was preferred under conditions of kinetic control. Thus reaction of benzobicyclo[4.1.0]hepten-2-ol (**7**) under mild conditions with aqueous sulfuric acid and ether at room temperature gave a mixture consisting of 40% 6-hydroxy-6,7-dihydro-5*H*-benzocycloheptene (**8**) and only 12%



7 8 9

(1) E. C. Friedrich, *J. Org. Chem.*, **34**, 528 (1969).
(2) E. C. Friedrich and R. L. Holmstead, *ibid.*, **36**, 971 (1971).
(3) A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1**, 1 (1965).
(4) W. G. Dauben, L Schutte, R. E. Wolf, and E. J. Deving, *J. Org. Chem.*, **34**, 2512 (1969).
(5) Radical **4** and its derivatives will be named and numbered for simplicity as derivatives of the bicyclo[4.1.0]heptenyl system rather than using the 1,1a,7,7a-tetrahydro-2*H*-cyclopropa[*b*]naphthalene nomenclature.
(6) S. Julia, M. Julia, and C. Hugnh, *Bull. Soc. Chim. Fr.*, 84 (1960).

2-hydroxymethyl-1,2-dihydronaphthalene (**9**). However, reaction of **7** under thermodynamic controlled conditions with acetic acid and concentrated sulfuric acid on a steam bath gave, after saponification of the acetate product, a 45% yield of 2-hydroxymethyl-1,2-dihydronaphthalene (**9**). Thus, since electronic factors which stabilize cations also stabilize the corresponding radicals, one might expect the cyclopropylcarbinyl–allylcarbinyl radical rearrangements in the benzobicyclo[4.1.1]heptene system to proceed preferentially with formation of the benzocycloheptadienyl radical (**6**).

As an entry into the benzobicyclo[4.1.0]hepten-2-yl radical system, we chose to use the same initial approach as we did with the cycloprop[2,3]indene system reported earlier,[2] *i.e.*, *via* free-radical α bromination of benzobicyclo[4.1.0]heptene (**10**). Besides studying the benzobicyclo[4.1.0]hepten-2-yl radical *via* free-radical α bromination procedures, it was also anticipated that free-radical organotin hydride reduction studies could be done on the cyclopropylcarbinyl and homoallyl bromides which we hoped to obtain as products from the bromination studies.

Results and Discussion

Bromination of Benzobicyclo[4.1.0]heptene (10).—A pure sample of benzobicyclo[4.1.0]heptene was prepared by Simmons–Smith[7] methylenation of 1,4-dihydronaphthalene. The free-radical NBS α bromination of **10**, using light as the initiator and a 1:1 mole ratio of **10** to NBS, proceeded smoothly at 26°. However, this procedure proved to be unsatisfactory for our purposes due to the formation of a considerable amount of the 2,5 dibromination product **11**. Although this compound could not be isolated and its structure proved directly, its formation was evidenced by its transformation into 2-(bromomethyl)naphthalene (**12**) upon standing or heating. This rearrangement presumably occurs *via* an ion-pair mechanism and its justification may be seen by consideration of the results of Julia and coworkers.[6] They observed that, when benzobicyclo[4.1.0]heptene-2,5-diol was treated with a 45% sulfuric acid solution in ether at room temperature for 6 hr, 2-(hydroxymethyl)naphthalene was obtained in a 62% yield after recrystallization. 1-Hydroxy-2-hydroxymethyl-1,2-dihydronaphthalene was proposed by Julia and coworkers as an intermediate, although it was not isolated.

(7) (a) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959); (b) E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964); (c) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

Because of the problem encountered using a 1:1 mole ratio of **10** to NBS, a 2:1 mole ratio was used in further studies. Also, the reactions were not carried to completion, but were stopped before all of the NBS had reacted. The results of the bromination reactions are given in Table I. The free-radical mechanism for the formation of the products of bromination of **10** should be analogous to that given earlier[1] for the bromination of cycloprop[2,3]indene.

TABLE I

NBS BROMINATION OF BENZOBICYCLO[4.1.0]HEPTENE (**10**) USING LIGHT INITIATION[a]

Starting material, mmol		Convn[b] of **10**,	Temp,	Yield of products,[c] %				
10	NBS	%	°C	**13**	**14**	**15**	**11**	Unknown
1	1	95[d]	26	14	66	0	15	5
2	1	42	26	73	16	0	4	7
2	1	42	5	90	6	0	2	2

[a] All reactions were complete in 1.25 hr. [b] Based on starting **10**. [c] Based on reacted **10**; the results of duplicate runs. [d] The reaction mixture was allowed to stand for a period of 4 hr at room temperature after completion of the bromination.

Controls were carried out which showed that the initially formed cyclopropylcarbinyl bromide **13**, which was identified by its characteristic nmr absorption peaks, was not stable under the reaction conditions. It rearranged on standing, presumably *via* an ion-pair type mechanism, to the more thermodynamically stable bromide **14**. The rearrangement was followed by nmr and shown to have a half life of *ca.* 2 hours at room temperature in the dark. Under the reaction conditions, *i.e.*, 26° and irradiating with light, the rearrangement of **13** to **14** was complete in less than 1 hr. Therefore, the amounts of compound **14** shown in Table I probably result mainly from the ion-pair rearrangement of the cyclopropylcarbinyl bromide **13** rather than from **14** being a direct product of the radical reaction. No evidence for compound **15** was found; and, if it is formed in the reaction, its yield is either less than or equal to the amount of unknown reported in Table I.

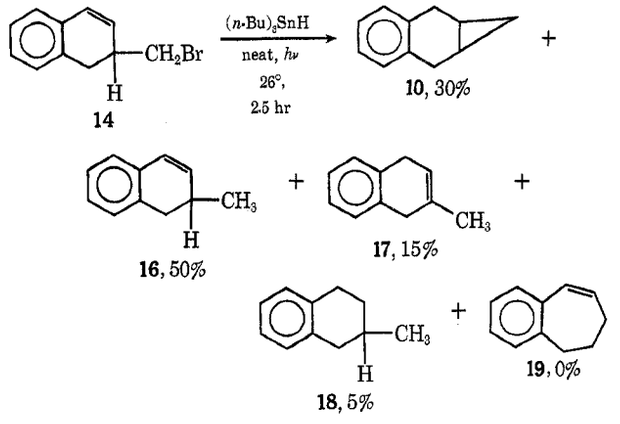
It is interesting to note that the nmr spectrum of 2-bromobenzobicyclo[4.1.0]heptene (**13**) in the reaction mixture showed only a single clean doublet at δ 5.7 (J = 2.5 Hz) for hydrogen attached to the carbon bearing the bromine atom rather than a pair of doublets due to exo and endo hydrogens, as was the case with the 1-bromocycloprop[2,3]indenes.[1] If both the exo and endo isomers are formed, either one predominates greatly or their absorptions occur at the same place with identical coupling.

Thus, in the NBS bromination of benzobicyclo[4.1.0]heptene (**10**) little can be said concerning the free-radical rearrangements of the initially formed cyclopropylcarbinyl radical **4**. If any rearrangement of the radical **4** does occur, it is probably to the primary homoallyl radical **5**, since no evidence for rearrangement to the secondary radical **6** was observed. However, one can say that bromination of **10** is very selective, giving primarily the cyclopropylcarbinyl bromide **13**. In fact it appears to be even more selective than the bromination of cycloprop[2,3]indene described earlier.[1,2]

With the hope of obtaining more information regarding free-radical rearrangements in the benzobicyclo[4.1.0]heptenyl system, we decided next to carry out organotin hydride reductions on the bromination products obtained.

Organotin Hydride Reductions.—Due to the problems of stability encountered with cyclopropylcarbinyl bromide **13**, reductions of this material could not be carried out. We were, however, able to obtain a pure sample of 2-(bromomethyl)-1,2-dihydronaphthalene (**14**) by the procedure reported in the Experimental Section. Thus, free-radical reductions were carried out on this material with tri-*n*-butyltin hydride.

The reductions were carried out using equimolar amounts of **14** and tri-*n*-butyltin hydride for 2.5 hr with photoinitiation and gave a 100% yield of hydrocarbon products based on reacted bromide **14**. The results, which are shown below, are the average values from experiments carried out in triplicate. The per cent yields shown are reproducible to *ca.* ±1%. The products were identified in the case of **10** and **16** by nmr analysis as described in the Experimental Section. As



is seen, a significant yield (30%) of benzobicyclo[4.1.0]-heptene (**10**) is formed. This can be compared to the 13% yield of cycloprop[2,3]indene formed when 1-bromomethylindene is reduced under the same conditions.[2]

Along with the normal reduction products, at least two other hydrocarbon products were obtained. On the basis of its mass spectrum one of the unknown compounds, obtained in 5% yield, was postulated to be 2-methyl-1,2,3,4-tetrahydronaphthalene (**18**). The mechanism for its formation is not readily apparent, however. The other product, obtained in 15% yield, is postulated to be 2-methyl-1,4-dihydronaphthalene (**17**) on the basis of its mass spectrum. The mechanism for the formation of **17** should be analogous to that postulated earlier for the formation of 3-methylindene[2] in the organotin hydride reductions of 1-bromomethylindene.

Finally, it is seen that benzosuberene (**19**), if formed at all, is present only in extremely small quantities. This result indicates that in this system, as well as in the cycloprop[2,3]indene system, cyclopropylcarbinyl–allylcarbinyl ring opening favors formation of the primary homoallyl radical over the secondary radical. The results also indicate that the postulated[1,2] electron-withdrawing inductive effect of the phenyl substituent in the cycloprop[2,3]indene system most likely has very little, if anything, to do with the direction of ring opening. Thus, the direction of ring opening probably depends mainly upon overlap between the orbital containing the odd electron and the adjacent orbitals of the cyclopropane ring leading to the primary radical being most favorable, as proposed by Dauben[4] for the 2-hydroxybicyclo[*n*.1.0]alk-2-yl radicals. In order to investigate this phenomenon in more detail, cyclopropylcarbinyl radical rearrangement studies in the simple bicyclo[3.1.0]hexyl and bicyclo[4.1.0]heptyl systems were carried out as are described in the following paper. In these two systems there are no electronic or steric complications caused by a phenyl or other substituent which might affect the direction of ring opening.

Experimental Section

Boiling points are uncorrected. Mass spectra were run on a CEC Model 21-104 single-focusing instrument by Mr. J. Voth. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

Nuclear Magnetic Resonance Spectra.—All nmr data were obtained using procedures similar to those described earlier[1,2] for the free-radical studies in the cycloprop[2,3]indene system.

Glpc Analyses.—Gas–liquid phase chromatographic (glpc) analyses were carried out using an Aerograph A90-P3 instrument equipped with a Pyrex injector insert. Separation of the bromination products was carried out on a 5 ft × 0.25 in. stainless steel column with a 20% SE-30 on 60/80 mesh Chromosorb W packing. The temperature of the column was maintained at 150° while the helium flow rate was at 60 ml/min. The retention times in minutes of the various compounds encountered were, benzobicyclo[4.1.0]heptene, 6; 2-bromomethyl-1,2-dihydronaphthalene, 20; and 2-bromomethylnaphthalene, 30. Analysis of the hydrocarbon products was carried out on three different columns: (1) a 2 m × 0.25 in. copper column with a 20% di-*n*-decylphthalate on 80/100 mesh Chromosorb W packing, with column temperature maintained at 120° and a helium flow rate of 86 ml/min—retention times in minutes of the various hydrocarbons encountered were, 2-methyl-1,2-dihydronaphthalene, 2-methyl-1,2,3,4-tetrahydronaphthalene, and 2-methyl-1,4-dihydronaphthalene, 24; benzobicyclo[4.1.0]heptane, 30; and benzosuberene, 56; (2) a 2 m × 0.25 in. copper column with 20% 3-nitro-3-methylpimelonitrile (NMPN) on 80/100 mesh Chromosorb W packing, with the temperature maintained at 100° and a helium flow rate of 47 ml/min—retention times in minutes on this column were, 2-methyl-1,2,3,4-tetrahydronaphthalene, 20; 2-methyl-1,2-dihydronaphthalene, 24; 2-methyl-1,4-dihydronaphthalene, 27; and benzobicyclo[4.1.0]-heptene, 29; (3) a 4 ft × 0.125 in. column with a 20% Carbowax 20M on 80/100 mesh Chromosorb W packing; temperature was maintained at 150° and helium flow rate at 30 ml/min—the retention times in minutes of the various hydrocarbon products were 2-methyl-1,2,3,4-tetrahydronaphthalene, 11; 2-methyl-1,2-dihydronaphthalene, 13; 2-methyl-1,4-dihydronaphthalene, 14; and benzobicyclo[4.1.0]heptene, 15.5.

Photolysis Equipment.—The light-initiated experiments were carried out using a 275-W G. E. sun lamp placed approximately 10 cm from the object being irradiated. All glassware used was Pyrex.

Preparation of 1,4-Dihydronaphthalene.—This material was prepared by the method of Ivanoff and Markov.[8] The reaction

(8) C. Ivanoff and P. Markov, *Naturwissenschaften*, **50**, 688 (1963).

of 19 g (0.78 mol) of powdered magnesium and 75 g (0.58 mol) of naphthalene in 1 l. of liquid ammonia gave, after work-up and distillation, 59 g of a mixture consisting of *ca.* 88% of 1,4-dihydronaphthalene (81.5% theory) and *ca.* 12% of naphthalene. Removal of the naphthalene was accomplished by the procedure of Sand and Gensler[9] using 30 g of the above mixture and 74 g (0.286 mol) of mercuric acetate. Distillation, after work-up, gave 12.2 g (46% recovery) of pure 1,4-dihydronaphthalene: bp 80–82° (*ca.* 8.5 mm); n^{24}D 1.5587 [lit.[10] bp 84° (9.5 mm); n^{33}D 1.5549]; nmr (CCl_4) δ 2.7 (s, 4 H), 5.35 (s, 2 H, vinyl), and 6.4–6.7 ppm (multiplet, 4 H, aromatic).

Preparation of Benzobicyclo[4.1.0]heptene (10).—Compound **10** was prepared using the LeGoff[11] modification of the Simons–Smith procedure. The zinc–copper couple was prepared using 0.8 g of cupric acetate monohydrate, 90 ml of glacial acetic acid, and 50 g (0.76 mol) of 30-mesh zinc granules. The couple was added to a 1-l. three-necked flask fitted with a dropping funnel and containing 200 ml of anhydrous ether. The mixture was stirred mechanically and heated to reflux. To the refluxing solution was added 60 g (0.34 mol) of dibromomethane and this mixture was allowed to reflux for 5–10 min. Then a solution containing 62 g (0.35 mol) of dibromomethane and 59 g of a mixture of 1,4-dihydronaphthalene (*ca.* 88%) and naphthalene was added dropwise to the flask over a period of 2 hr. This mixture was refluxed for 46 hr, after which time the solution became very pink and viscous. Normal work-up procedures were then carried out yielding a solution which, upon distillation through a 60-cm spinning band column, gave 15 g (26% isolated yield) of pure benzobicyclo[4.1.0]heptene: bp 93° (11 mm); nmr (CCl_4) δ 0.3 (m, 2 H, cyclopropyl, J = 5 Hz), 1.3 (m, 2 H, cyclopropyl), 3.0 (s, 4 H, benzylic), and 6.8 ppm (m, 4 H, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 144 (48), 129 (100), 128 (43), 116 (37), 115 (26).

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.38. Found: C, 91.84; H, 8.42.

Bromination of Benzobicyclo[4.1.0]heptene Using NBS.—Into a 15 × 150 mm Pyrex test tube was weighed 0.432 g (3.0 mmol) of benzobicyclo[4.1.0]heptene, 0.267 g (1.5 mmol) of NBS, and 2 ml of CCl_4. A thermometer was inserted into the solution and the tube was irradiated while being stirred magnetically. Cooling was carried out by running tap water over the outside of the tube, or in the lower temperature reactions, by a cold brine solution. After 1.25 hr irradiation was stopped. The succinimide was filtered off, and an nmr spectrum of the solution was taken immediately. 2-Bromobenzobicyclo[4.1.0]-heptene (**13**) was readily identified by its characteristic absorptions in the nmr spectrum: nmr (CCl_4, reaction mixture) δ 0.6 (m, 2 H, cyclopropyl), 1.8 (m, 2 H, cyclopropyl), 3.4 (d, 2 H, benzylic, J = 4 Hz), 5.7 (d, 1 H, –CHBr–, J = 2.5 Hz), and 7.3 ppm (m, 4 H, aromatic).

Product Analyses in the Bromination Reactions.—In the bromination of benzobicyclo[4.1.0]heptene, the per cent yields of the bromide products were determined by nmr using the aromatic region (4 H) as the internal standard. Yields of the various products were calculated in the following manner. 2-Bromobenzobicyclo[4.1.0]heptene (**13**) was identified by the characteristic doublet of the –CHBr group at δ 5.7 (J = 2.5 Hz). The amount of 2-bromomethyl-1,2-dihydronaphthalene (**14**) was determined by observing the change in the vinylic proton region (δ 6.0 and 6.6) when the reaction mixture was heated at 80° for 30 min. The difference between the amount of vinylic absorption before and after rearrangement of the cyclopropylcarbinyl bromide **13** gave the amount of bromide **14** formed initially. The amount of dibromide **11** was calculated from the nmr absorption of the methylene protons (δ 4.7, 2 H) of 2-(bromomethyl)naphthalene (**12**), which was formed from the dibromide upon heating at 80° for 30 min. No evidence for compound **15** was observed.

2-(Bromomethyl)naphthalene (12).—A sample of this material was isolated by preparative glpc techniques from the bromination product mixture. After recrystalization from ethanol, it had a melting point of 54–55° (lit.[12] mp 54°). Its nmr and ir spectra were identical with those of an authentic sample of **12** prepared by the method of Chapman and Williams[12] from NBS bromination of 2-methylnaphthalene in CCl_4 solution at reflux in the presence of benzoyl peroxide initiator: nmr (CCl_4) δ 4.7 (s, 2 H, CH_2Br) and 7.9 ppm (m, 7 H, aromatic).

Preparation and Isolation of 2-Bromomethyl-1,2-dihydronaphthalene (14).—Bromination, as previously described, was carried out on benzobicyclo[4.1.0]heptene (**10**). Removal of the CCl_4 solvent by distillation was carried out on the final reaction mixture. The remaining yellow mixture was then separated into its various components by preparative glpc. 2-Bromomethyl-1,2-dihydronaphthalene was collected from the 1-m SE-30 column previously described. The slightly yellow liquid (n^{24}D 1.6055) was identified by nmr: nmr (CCl_4) δ 2.6 (m, 1 H), 2.8 (s, 2 H, benzylic), 3.2 (d, 2 H, $-CH_2Br$, J = 7 Hz), 6.0 (q, 1 H, vinyl, J = 10, 4 Hz), 6.6 (d, 1 H, vinyl, J = 10 Hz), and 7.1 ppm (m, 4 H, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 224 (11), 222 (11), 143 (43), 142 (24), 141 (30), 129 (100), 128 (40), 115 (27).

Anal. Calcd for $C_{11}H_{11}Br$: C, 59.21; H, 4.96; Br, 35.81. Found: C, 59.51; H, 5.10; Br, 35.53.

Organotin Hydride Reductions of 2-Bromomethyl-1,2-dihydronaphthalene (14).—Into a polished glass nmr tube was weighed 0.223 g (1 mmol) of bromide **14** and 0.290 g (1 mmol) of tri-*n*-butyltin hydride. The mixture was then irradiated at 26°. Cooling was accomplished by running tap water over the tube. When the reaction was complete, and after spectra were taken, the mixture was distilled under vacuum through a micro apparatus to separate the hydrocarbon products. The hydrocarbon fraction was collected to a pot temperature of 120° (5 mm). The pot residue remaining consisted of tri-*n*-butyltin bromide. The hydrocarbons were then analyzed by nmr, glpc, and mass spectral techniques.

Product Analysis in the Organotin Hydride Reductions of 2-Bromomethyl-1,2-dihydronaphthalene (14).—In the tri-*n*-butyltin hydride reductions of **14**, the per cent yields of hydrocarbons were obtained by nmr examination using the aromatic region (4 H) as an internal standard as follows. The yield of benzobicyclo[4.1.0]heptene was determined by using the integration of its singlet at δ 3.0 (4 H). The relative yields of benzobicyclo[4.1.0]heptene, 2-methyl-1,2-dihydronaphthalene (**16**), 2-methyl-1,2,3,4-tetrahydronaphthalene (**18**), and 2-methyl-1,4-dihydronaphthalene (**17**) were then determined by glpc analysis as described below. The actual yields of **16**, **17**, and **18** were then calculated using the previously calculated yield for benzobicyclo[4.1.0]heptene obtained by nmr analysis.

The hydrocarbon mixture was first injected into the didecylphthalate glpc column. Two peaks emerged and the corresponding hydrocarbons were collected. One was found to be benzobicyclo[4.1.0]heptene by comparison of its spectral properties with those of an authentic sample. The other peak collected was found to be a mixture of hydrocarbons. This mixture was injected into the NMPN column previously described yielding three peaks which were collected. The major component was found to be 2-methyl-1,2-dihydronaphthalene (**16**): nmr (neat) δ 0.8 (d, 3 H, $-CH_3$, $-CH_3$, J = 7 Hz), 2.4 (m, 3 H, CH_2-CH–), 5.4 (d, 1 H, vinyl, J = 9 Hz), 6.05 (d, 1 H, vinyl, J = 9 Hz), and 6.7 ppm (s, 4 H, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 144 (35.5), 129 (100), 128 (35), 115 (11).

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.38. Found: C, 91.73; H, 8.28.

Another component was determined to be 2-methyl-1,2,3,4-tetrahydronaphthalene (**18**) by nmr analysis and comparison of its mass spectrum to the literature:[13] mass spectrum (70 eV) *m/e* (rel intensity) 146 (49), 131 (23), 117 (11.2), 104 (100), 91 (36).

The last component was postulated to be 2-methyl-1,4-dihydronaphthalene (**97**). The mass spectrum gave a parent ion of *m/e* 144: mass spectrum (70 eV) *m/e* (rel intensity) 144 (34.57), 130 (10.7), 129 (100), 128 (34.5), 115 (10.37).

Preparation of Benzosuberene (19).—The procedure used essentially follows that of Huisgen, *et al.*[14] Using 1 g (6.25 mmol) of benzosuberone, 0.95 g of the corresponding alcohol was prepared by reduction with lithium aluminum hydride. Dehydra-

(9) I. Sand and O. Gensler, *Ber.*, **36**, 3705 (1903).
(10) K. Von Anwers, *ibid.*, **46**, 2988 (1913).
(11) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
(12) N. B. Chapman and F. A. Williams, *J. Chem. Soc.*, 5044 (1952).
(13) "Mass Spectral Data Tables," American Petroleum Institute, Project 44, Serial No. 1211.
(14) R. Huisgen, E. Rauenbusch, G. Seidle, and I. Wimmer, *Justus Liebigs Ann. Chem.*, **671**, 41 (1964).

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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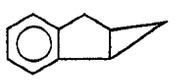
Received November 30, 1971

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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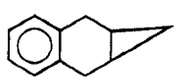

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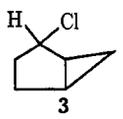
was noted that with both systems rearrangement of cyclopropylcarbinyl radicals to primary allylcarbinyl radicals proceeds in preference to rearrangement to secondary benzylic or simple secondary allylcarbinyl radicals, respectively. Based on the stabilities expected for the rearranged radical products,[3] 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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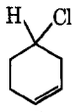

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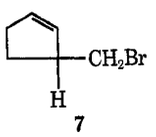

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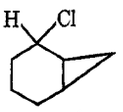

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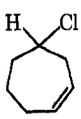

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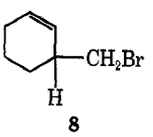

8

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.

(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.