acid-d_2 to **12** and **13** is again consistent with the structural assignments.

Apparently in the apobornene systems the normal rate of solvent capture is inhibited by the β-methyl steric effect and the 6,2-hydride shift becomes more than competitive.[8] This steric inhibition of solvation has recently been noted by Kleinfelter and Watsky in studies involving the 3-*exo*-phenyl-2-norbornyl cation intermediates.[9] In fact, they suggest that a 3-*exo*-phenyl group blocks the approach to a 2-norbornyl cation intermediate more effectively than a 7-*syn*-phenyl group does. Furthermore, they have observed in their studies of the 3-phenyl-2-norbornyl cation system,[9,10] that in unbuffered acetic acid (thermodynamically controlled conditions) products derived from the 1-phenyl-2-norbornyl cation are formed in substantial quantities, in agreement with the present study.

In summary, it appears that, under equilibration conditions, the initially formed tertiary and benzylic norbornyl cation derived from arylbornenes or arylapobornenes will also rearrange to yield products resulting from the capture of a secondary cation. The results with the arylapobornene system suggest that, when more than one interconvertible secondary site is available, acetates will be derived from the more accessible one.

Experimental Section

Analytical.—Nuclear magnetic resonance spectra were obtained on a Varian Associates Model A-60D spectrometer where the internal standard was tetramethylsilane. Galbraith Laboratories, Inc., Knoxville, Tenn., performed all the microanalyses. The melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

Reagents.—Acetic acid-d_1 (99.5%) and sulfuric acid-d_1 (99%) were obtained from Bio-Rad Laboratories. Apocamphor was synthesized according to the procedure developed by Brown, Kawakami, and Misumi.[11]

Synthesis of the Aryl Olefins 7, 12, and 13.—The aryl olefins were made by the Grignard reaction of the appropriate ketone and arylmagnesium halide to yield the corresponding aryl alcohol. These alcohols were directly dehydrated by stirring a few minutes with boron trifluoride etherate at room temperature. An attempted dehydration of **10** produced considerable phenylcamphene, as has been noted elsewhere.[12]

2-*p*-Anisylbornene (**7**) was recrystallized from cyclohexane to yield (almost quantitatively) pure **7**: mp 62–63°; nmr δ 5.85 (d, 1 H, $J_{3,4}$ = 3.0 Hz, vinyl H at C-3), bridgehead proton at H_4 centered at 2.44.

Anal. Calcd for $C_{17}H_{22}O$: C, 84.21; H, 9.15. Found: C, 84.37; H, 9.30.

2-*p*-Anisylapobornene (**12**) was purified by distillation, 45° (0.2 mm). This material subsequently solidified and was recrystallized from cyclohexane to yield 87% **12**: mp 44–45°; nmr δ 6.02 (d, 1 H, $J_{3,4}$ = 3.5 Hz, vinyl H at C-3), bridgehead protons at 2.60 and 2.30.

Anal. Calcd for $C_{16}H_{20}O$: C, 84.02; H, 8.83. Found: C, 84.03; H, 8.80.

2-Phenylapobornene (**13**) was likewise made from apocamphor and purified by distillation at 70° (0.1 mm) in a yield of 89%. An nmr spectrum exhibited the vinyl proton at C-3 at δ 6.08 with J = 3.0 Hz. The bridgehead hydrogens occur at δ 2.58 and 2.28. Difficulty was experienced in obtaining an acceptable microanalysis for **13** even though it appeared to be homogeneous by ir, nmr, tlc, and vpc techniques. In this instance, we purified and characterized the corresponding alcohol, *endo*-2-phenyl-*exo*-2-apobornanol. The alcohol distilled at 115° (0.2 mm).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.42; H, 9.63. Found: C, 83.30; H, 9.66.

4-Phenyl-2-*exo*-bornyl Acetate (**11**).—*endo*-2-Phenyl-*exo*-2-bornanol (**10**), 3.02 g (13.0 mmol), was dissolved in 50 ml of 0.18 *M* sulfuric acid in acetic acid and warmed to 40° for 30 hr. An nmr spectrum showed *ca.* 95% conversion to the title acetate in the recovered product (isolated as below). The product was recrystallized from cyclohexane, mp 84–85°.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.89. Found: C, 79.32; H, 8.97.

Acid-Catalyzed Addition of Acetic Acid to the Aryl Olefins 7, 12, and 13.—The procedure used is described for the formation of 4-*p*-anisyl-*exo*-2-bornyl acetate (**8**). 2-*p*-Anisylbornene (**7**), 3.50 g (1.5 mmol), was dissolved in 50 ml of 0.18 *M* sulfuric acid in acetic acid and warmed to 40° for 24 hr. Work-up consisted of an ether extraction where the extracts were washed with a 10% sodium bicarbonate solution. The ether extracts were dried (magnesium sulfate) and the solvent was removed under vacuum. An nmr spectrum on the crude product indicated *ca.* 95% conversion to the title acetate (**8**). The acetate was distilled, 75° (0.2 mm).

Anal. Calcd for $C_{19}H_{26}O_2$: C, 75.46; H, 8.67. Found: C, 75.39; H, 8.59.

The conversion of **12** to 1-*p*-anisyl-5,5-dimethyl-*exo*-2-norbornyl acetate (**14**) was accomplished at 40° in 24 hr. An nmr spectrum showed the crude product to be *ca.* 85% **14** with the remainder being an unidentified but presumably polymeric type material. The acetate was purified by thick layer chromatography using silica gel G and a 2:1 chloroform to carbon tetrachloride mixture as the eluent. The acetate **14** was then distilled at 70° (0.1 mm).

Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.18; H, 8.49.

The formation of 1-phenyl-5,5-dimethyl-*exo*-2-norbornyl acetate (**15**) was accomplished as above with the crude product being close to 95% **15**. Purification was by distillation at 70° (0.1 mm).

Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.51. Found: C, 79.04; H, 8.51.

Registry No.—**7**, 31059-45-7; **8**, 40635-57-2; **10**, 40548-30-9; **11**, 40548-31-0; **12**, 40548-32-1; **13**, 40548-33-2; **14**, 40548-34-3; **15**, 40548-35-4; camphor, 76-22-2; apocamphor, 514-15-8; *endo*-2-phenyl-*exo*-2-apobornanol, 40548-36-5; acetic acid, 64-19-7.

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Thermal Rearrangements of Bicyclo[3.1.0]hex-2-ene. Conversion of 3-Deuteriobicyclo[3.1.0]hex-2-ene to 1,3- and 1,4-Cyclohexadiene-d_1

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Detailed investigations[1] of the automerization of bicyclo[3.1.0]hex-2-ene have included studies of the reactivity at temperatures where nondegenerate pro-

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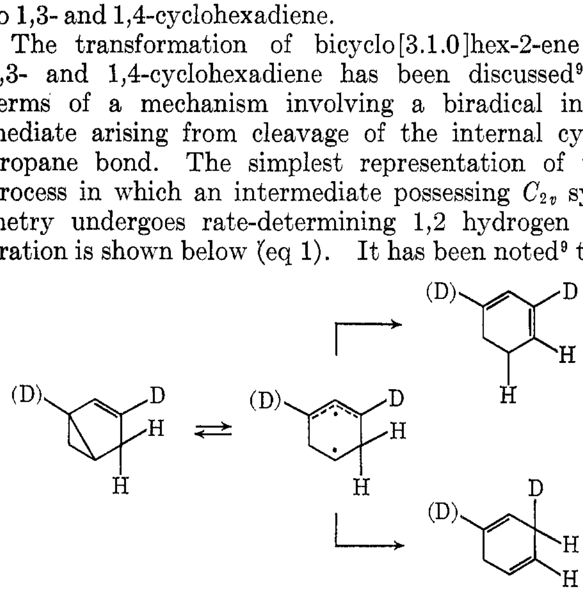
[1] R. S. Cooke and U. H. Andrews, unpublished results.

cesses are important. Current controversy[2-8] over the mechanism of the isomerization of bicyclo[2.1.0]pent-2-ene to cyclopentadiene prompts a report concerning the rearrangement of bicyclo[3.1.0]hex-2-ene to 1,3- and 1,4-cyclohexadiene.

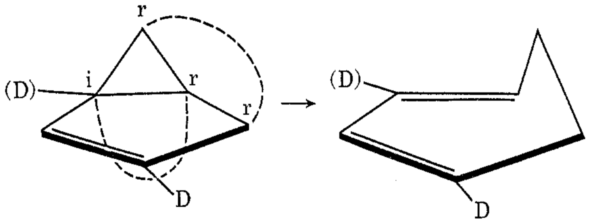
The transformation of bicyclo[3.1.0]hex-2-ene to 1,3- and 1,4-cyclohexadiene has been discussed[9] in terms of a mechanism involving a biradical intermediate arising from cleavage of the internal cyclopropane bond. The simplest representation of this process in which an intermediate possessing C_{2v} symmetry undergoes rate-determining 1,2 hydrogen migration is shown below (eq 1). It has been noted[9] that



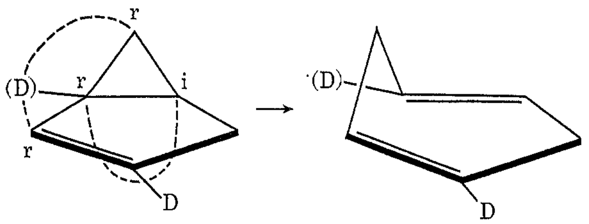
(1)

1,3-cyclohexadiene might also arise upon 1,4 hydrogen migration.

An alternative mechanism effecting these transformations is an orbital symmetry allowed $_{\sigma}2_s + {}_{\sigma}2_a$ process not requiring hydrogen migration (eq 2 and 3).



(2)



(3)

The relative importance of the $_{\sigma}2_s + {}_{\sigma}2_a$ and biradical mechanisms may be estimated by examination of the deuterium distribution in the cyclohexadienes-d_1 formed in the pyrolysis of 3-deuteriobicyclo[3.1.0]hex-2-ene. Since deuterium is scrambled in the bicyclic material much faster than isomerization occurs,[10] one may consider rearrangement of a species with one-half deuterium atom in the C_1 and C_3 positions.

In a typical experiment, 0.180 ml of 3-deuteriobicyclo[3.1.0]hex-2-ene, with 0.874 ± 0.006 deuterium atoms at the C_3 position and none elsewhere, was pyrolyzed in a well-seasoned plug-flow reactor at a nominal temperature of 432 ± 1°. Nitrogen was used as the carrier gas and the nominal residence time was 15.2 ± 0.5 sec. Recovered material contained bicyclo[3.1.0]hex-2-ene-d_1 (0.358 ± 0.002), 1,4-cyclohexadiene-d_1 (0.162 ± 0.002), 1,3-cyclohexadiene-d_1 (0.381 ± 0.002), and benzene (0.100 ± 0.003). The products were separated and the pmr spectra were examined. A summary of the values of the allylic hydrogen/olefinic hydrogen ratio in 1,4-cyclohexadiene-d_1 expected for each mechanism and those found experimentally is shown in Table I.

TABLE I

PREDICTED AND EXPERIMENTAL ALLYLIC HYDROGEN/OLEFINIC HYDROGEN RATIOS IN 1,4-CYCLOHEXADIENE-d_1

Biradical mechanism 1,2 H	1.00[a]
$_{\sigma}2_s + {}_{\sigma}2_a$ mechanism	1.28
Experimental	0.992 ± 0.023
	0.985 ± 0.030

[a] The predicted ratio will probably be slightly less than that listed owing to the unknown primary deuterium isotope effect on the rate of conversion of this compound to benzene. See ref 9; S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, **63**, 985 (1967); I. Fleming and E. Wildsmith, *J. Chem. Soc. D*, 223 (1970).

At 100 MHz the signals due to the two types of olefinic hydrogens in 1,3-cyclohexadiene are not resolved. Treatment of the recovered 1,3-cyclohexadiene-d_1 with maleic anhydride gave the expected Diels-Alder adduct.[11] Examination of the pmr spectrum permitted determination of the deuterium distribution at each position in 1,3-cyclohexadiene-d_1. These results are shown in Table II. Examination of the dmr spectrum of the adduct verified that deuterium was statistically distributed in the recovered 1,3-cyclohexadiene-d_1.

TABLE II

PREDICTED AND EXPERIMENTAL HYDROGEN RATIOS IN BICYCLO[2.2.2]OCT-2-ENE-5,6-DICARBOXYLIC ANHYDRIDE-d_1

	Olefinic	Methine	Methylene
Biradical 1,4 H	1.00	2.560	2.280
1,2 H	1.00	2.280	2.560
$_{\sigma}2_s + {}_{\sigma}2_a$	1.00	2.280	2.560
Statistical distribution	1.00	2.123	2.000
Experimental	1.00	2.118 ± 0.038	2.002 ± 0.036
	1.00	2.157 ± 0.036	2.003 ± 0.035

Only a minor amount of the conversion of bicyclo[3.1.0]hex-2-ene to 1,4-cyclohexadiene could result from operation of the $_{\sigma}2_s + {}_{\sigma}2_a$ mechanism. The major pathway probably involves a biradical intermediate which suffers rate-determining 1,2-hydrogen shift. However, orbital symmetry allowed mechanisms which involve synchronous cleavage of the cyclopropane ring and hydrogen migration are also consistent with the present results. The most reasonable of these find analogy in the conversion of *cis*-1-methyl-

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2-vinylcyclopropane to *cis*-hexa-1,4-diene.[12,13] Owing to a rapid scrambling process in the product, no mechanistic statements may be made concerning the formation of 1,3-cyclohexadiene. The mechanism of the scrambling pathway presumably involves sequential [1,5]-sigmatropic shifts.[14–24]

Experimental Section

Preparation of 3-Deuteriobicyclo[3.1.0]hex-2-ene.—Cyclopenten-3-ol was prepared from cyclopentadiene using a slight modification of the procedure described by Allred, Sonnenberg, and Winstein.[25] Bicyclo[3.1.0]hexan-3-ol was prepared using a modification of the procedure of Winstein and Sonnenberg[26] employing the zinc–copper couple described by LeGoff.[27] The oxidation procedure of Corey and Dawson[28] was used to prepare bicyclo[3.1.0]hexan-3-one. The overall sequence was performed in 8.8% average yield.

A 4.023-g (41.9 mmol) sample[29] of bicyclo[3.1.0]hexan-3-one was reduced with 0.885 g (21.1 mmol) of lithium aluminum deuteride according to the procedure of Winstein and Sonnenberg.[26,30] Following work-up, the ether solution of 3-deuteriobicyclo[3.1.0]hexan-3-ol was concentrated to 30 ml by distillation employing a 15-cm Vigreux column.

A 250-ml three-necked flask was charged with 1.34 g (55.9 mmol) of sodium hydride and 50 ml of dry ether. The flask was fitted with a stirring bar, addition funnel, serum cap, and reflux condenser topped with a gas inlet–outlet system. The stirred slurry was heated to reflux under a nitrogen atmosphere for the entire course of the reaction. The solution of alcohol from above was added dropwise over 35 min. After 3 hr, 3.47 g (45.7 mmol) of carbon disulfide was added slowly by syringe. After an additional 3 hr, 9.25 g (65.0 mmol) of methyl iodide was added slowly by syringe. After an additional 11 hr, water was carefully added and the reaction mixture was washed with four 20-ml portions of water. The ether layer was dried over magnesium sulfate, filtered, and concentrated under vacuum. Bulb-to-bulb distillation at 0.005 mm gave 7.175 g of methyl 3-(3-deuteriobicyclo[3.1.0]hexyl)xanthate[31] as a clear yellow oil.

A 15-ml flask fitted with a short-path still was charged with the xanthate mixture. The material was heated in an oil bath at 186–190°. The pyrolysate was redistilled to give 2.077 g of 3-deuteriobicyclo[3.1.0]hex-2-ene boiling in the range 72–74°. The overall sequence from bicyclo[3.1.0]hexan-3-one was performed in 61.9% yield.

Final purification was achieved by preparative glpc on a 3.0 m × 4.5 mm 21% β,β′-oxydipropionitrile on Chromosorb P column at 50°. The material was compared with an authentic sample of bicyclo[3.1.0]hex-2-ene prepared by the method of Schnieder and Crawford.[32] Examination of the pmr spectrum[33] revealed 0.126 ± 0.006 residual protons at the C_3 position when the signal at δ 5.40 was compared with the signal at δ 5.96 due to the proton at the C_2 position. Examination of the dmr spectrum of 3-deuteriobicyclo[3.1.0]hex-2-ene in tetramethylsilane solution revealed a single resonance 1.88 ppm upfield from deuteriochloroform.

Preparation of Bicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride-d_1.—In a typical experiment, the method of Hammond and Warketin[13] was followed to prepare the adduct from 0.0730 g (0.744 mmol) of maleic anhydride and 0.0383 g (0.472 mmol) of 1,3-cyclohexadiene-d_1. Three recrystallizations from equal volumes of benzene and petroleum ether (bp 60–90°) gave 0.0278 g of adduct with a melting range of 142–146°. The pmr spectrum was examined, and the signals due to the olefinic, methine, and methylene protons were determined from the resonances centered at δ 6.24, 3.09, and 1.42, respectively. The dmr spectrum of a sample in benzene revealed three signals in the uncorrected ratio olefinic:methine:methylene of 1.00:0.94 ± 0.02:2.11 ± 0.09.

Pyrolysis of 3-Deuteriobicyclo[3.1.0]hex-2-ene.—The 50-ml reaction zone of the pyrolysis apparatus was a 10-cm section of 30-mm Pyrex tubing butted to inlet and outlet tubes of 11-mm Pyrex tubing. A 7-mm Pyrex tube serving as a concentric thermocouple well ran the entire length of the apparatus, permitting measurement of temperature throughout the reactor zone and minimizing dead space in the inlet and outlet tubes. The pyrolysis apparatus was centered in a 30 cm × 33 mm tube furnace so that temperature was constant to ±1° across the reaction zone. Temperature was controlled with a Variac and measured using a chromel–alumel thermocouple. Dry nitrogen was employed as the carrier gas and the flow rate was regulated by means of a needle valve. The flow rate was measured with a soap bubble flow meter at room temperature and corrected to the temperature of the reaction zone.

The pyrolysis tube was washed with 15% ammonium hydroxide and air dried. Conditioning was achieved by pyrolysis of numerous samples of bicyclo[3.1.0]hex-2-ene under the conditions of the experiment. In a typical experiment, a sequence of nine 0.020-ml samples of 3-deuteriobicyclo[3.1.0]hex-2-ene were introduced into the system through a serum cap. The pyrolysate was condensed in a trap cooled in liquid nitrogen and transferred to storage ampoules using standard vacuum line techniques. In all cases, the recovery of material was close to quantitative.

The pyrolysate was analyzed by glpc on a 9.1 m × 2.0 mm 25% β,β′-oxydipropionitrile on a Chromosorb W column at 55°. Separation of the four components was achieved by preparative glpc on a 3.0 m × 4.5 mm 21% β,β′-oxydipropionitrile on Chromosorb P column at 50°. The pmr spectrum of 1,4-cyclohexadiene-d_1 was examined and the signals due to the olefinic and allylic protons were determined from the resonances centered at δ 5.72 and 2.68, respectively. In 1,3-cyclohexadiene-d_1, these resonances were centered at δ 5.88 and 2.18, respectively.

Registry No.—3-Deuteriobicyclo[3.1.0]hex-2-ene, 40387-26-6; lithium aluminum deuteride, 14128-54-2; bicyclo[3.1.0]hexan-3-one, 1755-04-0; 3-deuteriobicyclo[3.1.0]hexan-3-ol, 40387-28-8; methyl 3-(3-deuteriobicyclo[3.1.0]hexyl)xanthate, 40387-29-9; bicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic anhydride-d_1, 40386-99-0; 1,4-cyclohexadiene-d_1, 40531-27-9; 1,3-cyclohexadiene-d_1, 40387-00-6.

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