Huyser, Bredeweg, and Van Scoy[4,5] in explaining increased decomposition rates of di-*tert*-butyl peroxide in primary and secondary alcohols and amines.

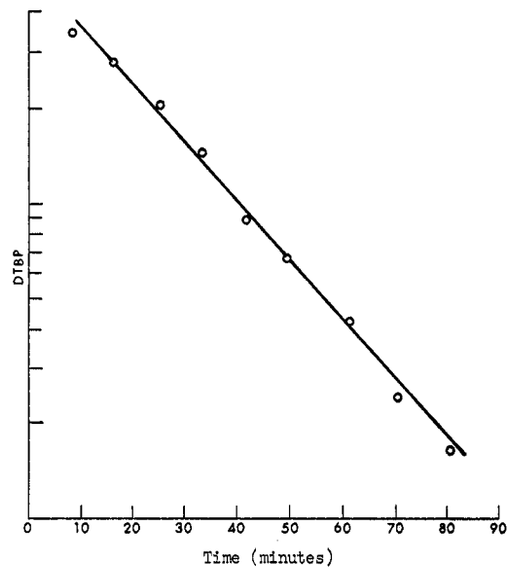

Figure 1.—First-order plot for the decomposition of di-*tert*-butyl peroxide (DTBP) in benzene with 0.043 mmol of L_3RhCl, 600 psig H_2, 20 mg of Ph_3P, 120°.

Experimental Section

Materials.—Except for the metal systems, commercial materials were used in this work: benzene, triphenylphosphine, tetralin, phenol, *m*-cresol, and Ionol. The following metal complexes were prepared as previously described: $(Ph_3P)_3RhCl$,[6,7] $(Ph_3P)_3RhBr$,[7] $(Ph_3P)_2CORhCl$,[7] $(Ph_3P)_4RhH$,[8] and $(Ph_3P)_3RuCl_2$.[9]

Decomposition of Di-*tert*-butyl Peroxide.—A solution of 0.79 g (5.4 mmol) of di-*tert*-butyl peroxide, 0.020 g (0.076 mmol) of Ph_3P, and 30 ml of benzene was charged in a nitrogen atmosphere to an 80-ml Inconel magnetically stirred autoclave (total free space including system, 126 ml). A pressure of 600 psig hydrogen was charged to the vessel. The temperature (120°) was maintained ±1% by a thermostatically controlled heating mantle. In experiments using metal catalysts, 0.043 mmol of catalyst was also added to the reaction solution. In experiments in which $(Ph_3P)_3RhCl$ concentrations were varied, 0.021, 0.06, and 0.09 mmol of catalyst were employed. The reaction mixture was analyzed by standard glc techniques for di-*tert*-butyl peroxide, *tert*-butyl alcohol, and acetone.

Decomposition of Di-*tert*-butyl Peroxide with Additives.—The above procedure and amounts of reactants were used and 0.5- or 1.0-g amounts of tetralin, phenol, *m*-cresol, or Ionol were also added. Glc analysis showed no loss of *m*-cresol in *m*-cresol experiments.

Registry No. —*tert*-Butyl alcohol, 75-65-0; *tert*-butyl peroxide, 110-05-4.

Acknowledgment.—The authors are grateful to Dr. L. H. Gale and Dr. H. V. Holler for helpful discussions.

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The Acid-Catalyzed Addition of Acetic Acid to 2-Arylbornenes and 2-Arylapobornenes

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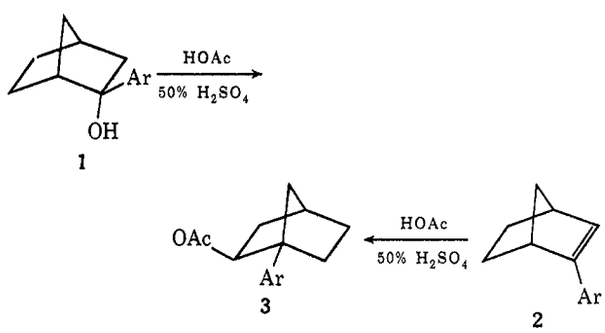
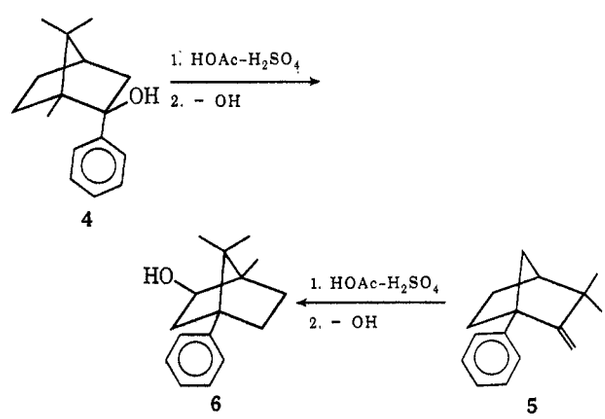
Received January 31, 1973

Ample results from product studies involving arylnorbornyl cationic intermediates have shown that the thermodynamically controlled product is often derived from a rearranged cation. An example that illustrates the above is the rearrangement observed in the interaction of 2-*exo*-aryl-2-*endo*-norbornanols (**1**) and 2-arylnorbornenes (**2**) with acetic acid in the presence of sulfuric acid to yield 1-aryl-*exo*-2-norbornyl acetates (**3**).[1]



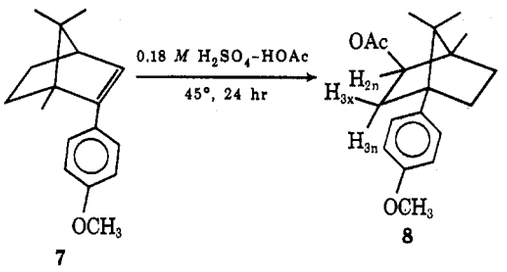
One of the more intriguing results of this type is the reported rearrangement of 2-*endo*-phenyl-2-*exo*-borneol (**4**) and 1-phenylcamphene (**5**) to produce 4-phenylisoborneol (**6**).[2] Obviously a gross structural reorganization has taken place, although the final product is again derived from a secondary norbornyl cation.



These earlier observations can be readily confirmed by utilizing nmr structural assignments. Thus, the treatment of 2-*p*-anisylbornene (**7**) with acetic acid and sulfuric acid under rigorous conditions produced almost exclusively 4-*p*-anisyl-2-*exo*-bornyl acetate (**8**).

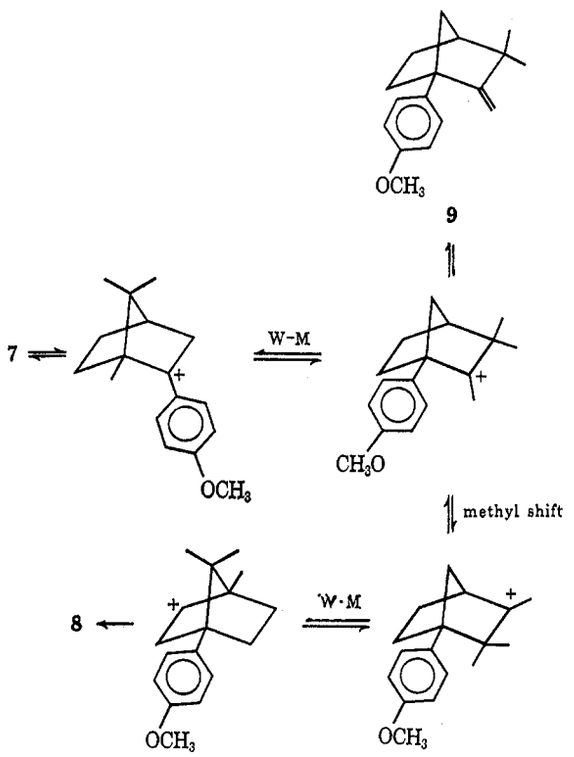
When the reaction was carried out with the same reagent at 25° for 0.5 hr, the only product isolated was

(1) For an excellent review on these and related rearrangements involving arylnorbornyl cations, see D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960.
(2) (a) J. Bredt, *J. Prakt. Chem.*, **98**, 96 (1918); (b) S. Nametkin, A. Kitschkin, and D. Kurssanoff, *ibid.*, **124**, 144 (1930); (c) S. Leduc, *C. R. Acad. Sci.*, **180**, 1502 (1925).



7 8

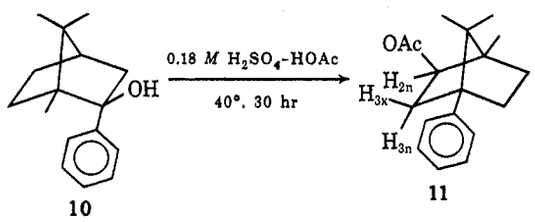
1-*p*-anisylcamphene (**9**). The intermediate **9** was slowly converted to **8** under the milder reaction conditions. A rearrangement scheme consistent with the formation of **8** and **9** is one involving a 3,2-methyl



shift.[3] An analogous scheme accounts for many aspects of the formolysis of the 2-*p*-anisylcamphenilols.[4]

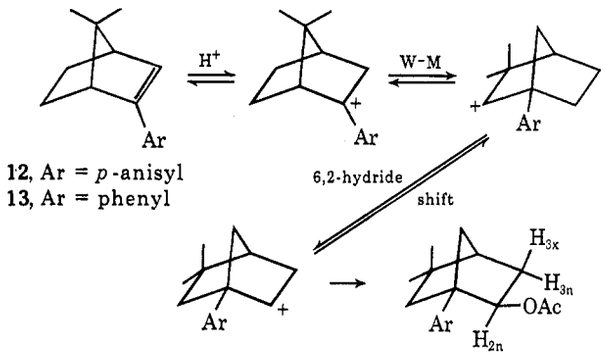
It is interesting to note that again rearrangements occur until a secondary norbornyl cation can be trapped, and acetates derived from the capture of a benzylic or tertiary norbornyl cation are apparently very labile and are not observed.

When the alcohol *endo*-2-phenyl-*exo*-2-bornanol (**10**) was treated directly with the acetic acid reagent the final product was again 4-phenyl-*exo*-2-bornyl acetate (**11**). When this acetolysis was carried out in acetic acid-d_1 and sulfuric acid-d_2, extensive deuterium incorporation occurred in the methyl groups as well as at C-3. Dideuteration at C-3 was evidenced by the complete collapse of the multiplet for H_{2n} and offers support for the structural assignment. The deuterium incorporation into the methyl groups occurred to approximately 67% and is consistent with a methyl shift and equilibration with the camphene intermediate. It was not possible to distinguish precisely the deuterium fraction in each of the methyls, although there appeared to be deuterium in all three methyls in spite of the known preference for exo methyl shifts.[3,5,6]



10 11

The complications associated with the arylbornene to arylcamphene rearrangement can be avoided in the 2-arylapobornene systems **12** and **13** where the bridgehead methyl is lacking. Treatment of the olefins **12** and **13** under similar thermodynamically controlled conditions again produced a rearranged secondary acetate whose structure is assigned to the 1-aryl-5,5-dimethyl-*exo*-2-norbornyl acetates **14** and **15**, respectively. A Wagner–Meerwein rearrangement followed by a 6,2-hydride shift can account for the formation of **14** and **15**.



12, Ar = *p*-anisyl
13, Ar = phenyl

14, Ar = *p*-anisyl
15, Ar = phenyl

The final acetates **14** and **15** are not derived from the first formed secondary carbonium ion intermediate but instead from a more accessible secondary norbornyl cation (not flanked by geminal dimethyls). This β-methyl steric effect has been noted previously by Berson[7] in his thorough study of hydride shifts in methylnorbornyl cations.[5,7] Also, no products could be detected in this instance that would be derived from a methyl shift as observed in the bornene systems. The nmr parameters for the bornene and apobornene systems are listed in Table I. Deuterium incorporation observed in the addition of acetic acid-d_1 and sulfuric

TABLE I

NMR SPECTRA[a] OF ACETATES **8**, **11**, **14**, AND **15**

Compd	Chemical shift,[b] ppm, for H_{2n}	Observed splittings, Hz[c] $J_{2n,3n}$	$J_{2n,3x}$
8	4.75 (dd)	8.0	3.5
11	4.75 (dd)	8.0	4.0
14	4.88 (dd)	8.0	3.5
15	4.94 (dd)	7.0	3.5

[a] Correct integration obtained for structure as listed. [b] In δ units, TMS internal reference, $CDCl_3$ solvent, at 60 MHz. [c] Long-range interaction less than 1 Hz.

(3) For examples of methyl shifts in closely related systems, see D. L. Adams and W. R. Vaughan, *J. Org. Chem.*, **37**, 3906 (1972), and references cited therein.

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(6) However, for an example of an endo 3,2-methyl shift, see S. Rengaraju and K. D. Berlin, *Tetrahedron*, **27**, 2399 (1971).

(7) J. A. Berson, A. W. McRowe, and R. G. Bergman, *J. Amer. Chem. Soc.*, **89**, 2573 (1967).

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 $C_{18}H_{24}O_2$: 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.

Acknowledgment.—We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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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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Received March 15, 1973

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-

(1) R. S. Cooke and U. H. Andrews, unpublished results.