Photochemical Transformations of Small Ring Carbonyl Compounds. XXXIX. Photochemical Synthesis and Chemical Reactivity of the Tricyclo[3.2.0.0^{2,6}]heptan-7-ol System[1]

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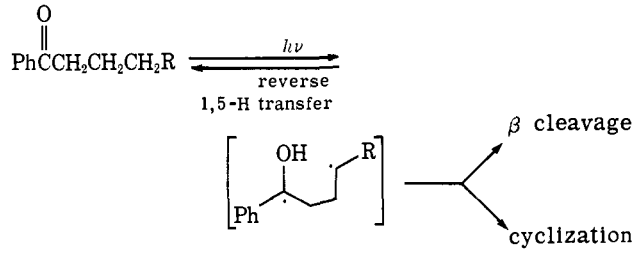
Abstract: The photolysis in benzene of *exo*-5-benzoylbicyclo[2.1.1]hexane (**4**) has been found to afford Δ^2-cyclopentenylacetophenone (**5**) and 7-phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol (**6**). The formation of these products is considered to proceed through a diradical intermediate formed by transannular hydrogen abstraction by the excited n–π^* triplet state. The tricyclic alcohol was found to rearrange thermally to **4** and **5**. The rearrangement to **4** was shown to proceed *via* cleavage of the bridgehead carbon–carbon bond followed by 1,5-H transfer. In basic media the tricyclic alcohol isomerized to *exo*-5-benzoylbicyclo[2.1.1]hexane with overall retention of configuration. The tricyclic alcohol was also found to be extremely unstable to acidic conditions and rearranged to 2-phenyl-*anti*-7-norbornenol. The rearrangement was rationalized as proceeding *via* a tricyclo[3.2.0.0^{2,7}]heptyl cation.

The type II photoelimination and cyclization reactions of aryl alkyl ketones having a γ hydrogen have been the subject of extensive investigations.[3-12] These reactions are believed to involve a 1,4-biradical intermediate, formed by γ-hydrogen abstraction by the carbonyl n–π^*[3] excited state. The biradical intermediate may either cyclize, undergo cleavage, or revert to starting ketone by reabstraction of hydrogen. The lines of evidence implicating the reversibility of the hydrogen transfer step are based on kinetic data[4,13] and are reinforced by stereochemical[14,15] and deuterium isotope effects.[16-18] The quantum efficiencies for product formation are determined by the partitioning of the biradical intermediate. The factors which govern the relative rate constants for cyclization and elimination of the 1,4 biradical have recently attracted attention.[4,5,19-22] It is generally agreed that the most favorable transition state for β cleavage of the biradical is



one in which maximum overlap occurs between the developing π orbitals and the π orbitals at the radical centers. This requires the radical centers to be parallel to the 2,3-C–C bond. The requirement for cyclobutanol formation is not expected to be so dependent upon the orientation of the 2,3 bond, and hence a high cyclobutanol to fragmentation ratio will be expected of ketones in which the 2,3 bond is held more or less rigidly in an orientation unfavorable to fragmentation. One of the earliest examples of this hypothesis is to be found in the photochemistry of phenyl cyclobutyl ketone (**1**),[19] which undergoes 60% cyclization to 2-phenylbicyclo[1.1.1]pentanol (**2**) and only 40% cleavage to the strain-free acyclic olefin **3**.[23] Another unusual

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(23) Several additional cases of ketones giving an unusually high proportion of cyclobutanols have been found and can be readily explained by the above hypothesis.[10,20,21,24-37]
(24) N. C. Yang and D. M. Thap, *Tetrahedron Lett.*, 3671 (1966).
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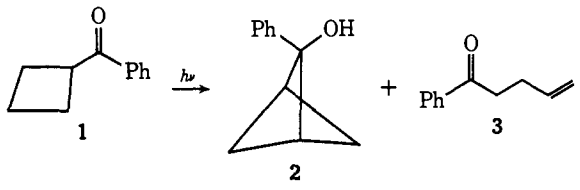
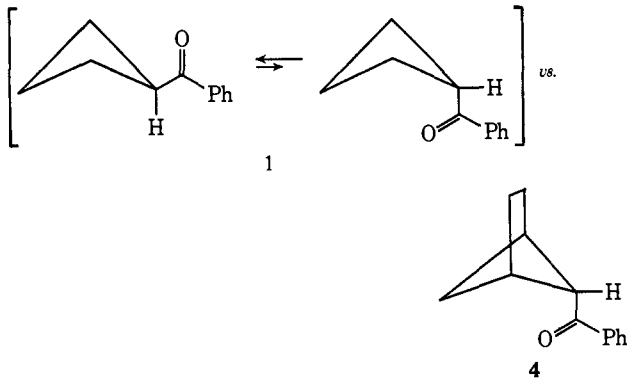
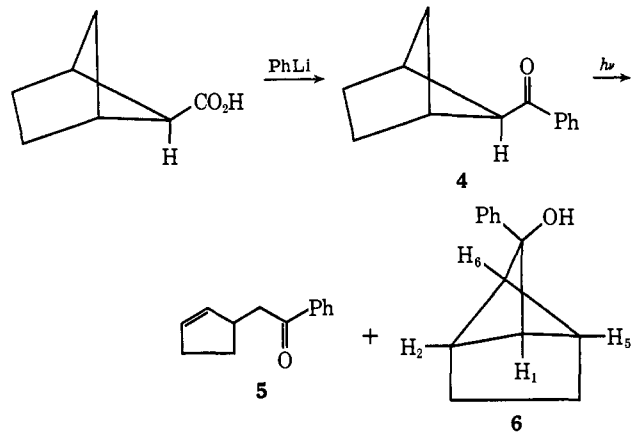


feature associated with the photochemistry of **1** is the dramatic inefficiency of internal hydrogen abstraction, both in terms of quantum yield ($\Phi = 0.03$) and reaction rate ($k_r = 5.5 \times 10^3$ sec^{-1}). The cyclobutane ring present in **1** is quite flexible and exhibits a dynamic ring-bending equilibrium which allows for conformation equilibration of monosubstituted cyclobutanes.[38] It was previously argued that one possible source of inefficiency in the cyclobutyl phenyl ketone system was the low concentration of the conformer having the benzoyl group in the pseudoaxial position.[19] In order to test for this possibility, we decided to investigate the photochemistry of *exo*-5-benzoylbicyclo[2.1.1]hexane (**4**).[39] Bicycloketone **4** is an appropriate model for the

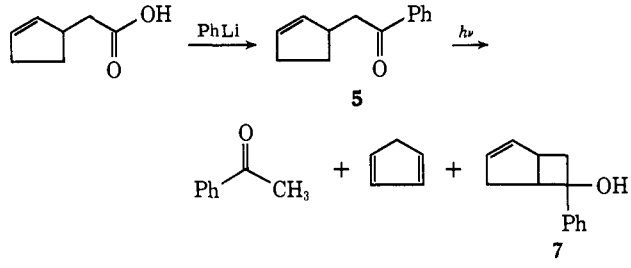


reactive conformer of cyclobutyl phenyl ketone, since the benzoyl group is now locked into the axial position. If the inefficiency of the cyclobutyl phenyl ketone system was totally due to the low population of the reactive conformer, then we would expect that **4** would be more reactive and would resemble valerophenone (the acyclic model) in terms of its photoefficiency and reactivity. The present paper reports on the photochemistry of *exo*-5-benzoylbicyclo[2.1.1]hexane and also describes the results of our thermal-, base-, and acid-catalyzed studies of the tricyclic alcohol formed from the irradiation of **4**. Mechanistic discussion is given in the accompanying paper which presents experimental evidence allowing characterization of the excited state and kinetic data which permit determination of the rate constants for the primary processes.

exo-5-Benzoylbicyclo[2.1.1]hexane (**4**), mp 58–59°, was readily prepared by the reaction of bicyclo[2.1.1]-hexane-*exo*-5-carboxylic acid[40] with phenyllithium. The spectral data and elemental analysis of this material are consistent with the assignment and are summarized in the Experimental Section. Its stereochemistry is clear from its nmr spectrum, which shows a 7.0 Hz long-range coupling constant between the distant endo C-5 and C-6 protons.[41] Irradiation of a 1% solution of **4** in benzene using a 450-W Hanovia lamp through a Pyrex filter for 2 hr led to the formation of two major photoisomers, shown to be Δ^2-cyclopentenylacetophenone (**5**, 79%) and 7-phenyltricyclo[3.2.0.0^{2,6}]-heptan-7-ol (**6**, 11%). The structure of the major



product (**5**), analogous to the ketoolefin produced photochemically from cyclobutyl phenyl ketone, is apparent from its spectral characteristics (see Experimental Section). Structure **5** was further confirmed by an independent synthesis from Δ^2-cyclopentenylacetic acid and phenyllithium. Extended irradiation of a solution of **4** in benzene gave, in addition to **5** and **6**, acetophenone, cyclopentadiene, and 6-phenylbicyclo[3.2.0]-hept-2-en-6-ol (**7**). Suspicion that the latter three compounds are secondary photoproducts was confirmed by the finding that the photolysis of **5** in benzene gave acetophenone (63%), cyclopentadiene, and **7** (5%).



These products can be readily rationalized by a Norrish type II cleavage of **5**. This process is analogous to that encountered by Meinwald on irradiation of campholenic aldehyde.[42]

The structure of tricyclic alcohol **6** (*p*-bromophenylurethane derivative, mp 137–138°) was elucidated on the basis of the physical and chemical data cited. The infrared spectrum shows hydroxyl bands at 2.86 and 3.04 μ and a carbon–oxygen stretching band at 8.32 μ. Its ultraviolet spectrum exhibited an absorption characteristic of an isolated benzene ring. The mass spectrum of **6** included peaks with *m/e* 186, 168, 120, 105, 91, and 77 and is very similar to that of **5**. Confirmation of the structure of **6** was available from its unique nmr spectrum. The 100-MHz nmr spectrum showed the aromatic hydrogens as a singlet at τ 2.75, the two bridgehead hydrogens (H_1 and H_6) as a singlet at τ

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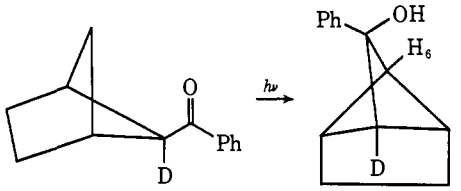
7.34, H_5 as a doublet at τ 6.45 (J = 7.0 Hz), H_2 as a doublet at τ 7.88 (J = 7.0 Hz), the hydroxyl proton as a broad singlet at τ 7.09, and the four methylenic hydrogens as an AB quartet (J = 10.0 Hz) centered at τ 8.31. The strong upfield shift of H_2 (relative to H_5) can be attributed to long-range shielding by the π electrons of the phenyl ring.[43]

The H_1–H_6 bridgehead–bridgehead long-range coupling in **6** was determined by the preparation of 7-phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol-1-*d* (**9**) *via* the ir-



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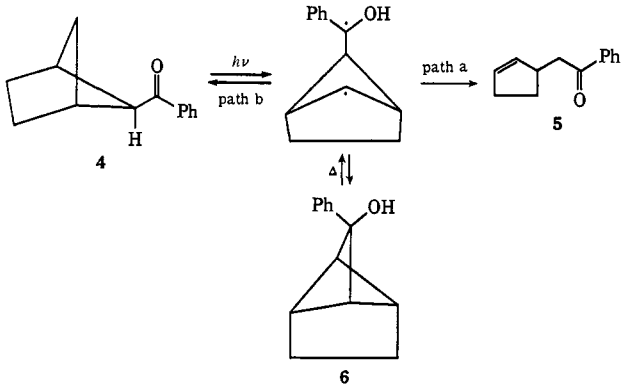
radiation of *exo*-5-benzoylbicyclo[2.1.1]hexane-5-*endo*-*d* (**8**). The nmr spectrum of the monodeuterated alcohol **9** showed a coupling constant of 2.70 Hz between the deuterium and bridgehead hydrogen. Since hydrogen–hydrogen coupling is as great by a factor of 6.55 as deuterium–hydrogen coupling,[44] the value obtained is essentially identical with that encountered in the bicyclo[1.1.1]pentane system (*i.e.*, J = 18.0 Hz)[45] indicating that the geometries of both ring systems are essentially the same.

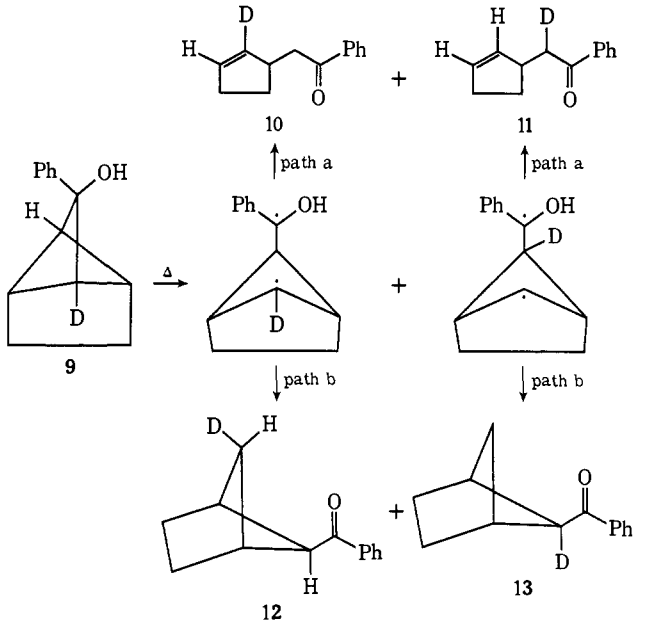
Thermal decomposition of **6** at 200° afforded a mixture of **4** (30%) and **5** (70%). The formation of these products can best be accounted for by a thermal cleavage of the bridgehead C–C bond followed by ring opening of the diradical (path a) or by a 1,5-H transfer step (path b). The formation of **5** and **6** from the irradiation of **4** may be considered to be analogous to the Norrish type-II cleavage and cyclobutanol formation observed with the irradiation of aliphatic ketones containing γ hydrogens. The behavior of the diradical generated by thermolysis of **6** is essentially the same as that encountered in the Norrish type-II process and once again illustrates the reverse hydrogen transfer step of 1,4 diradicals.[4,46–48]

Supporting evidence for the mechanism outlined in Scheme I was obtained by studying the thermal rearrangement of 7-phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol-1-*d* (**9**). If we neglect the isotope effect on the cleavage of the bridgehead carbon–carbon bond, then formation of Δ^2-cyclopentenylacetophenone would be expected to give equivalent amounts of **10** and **11**. Similarly, formation of *exo*-5-benzoylbicyclo[2.1.1]hexane *via* a 1,5-H transfer route would be expected to give comparable quantities of **12** and **13** (Scheme II). The products obtained from the thermolysis of **9** were isolated by vpc and were analyzed for their total deuterium content by mass spectroscopy. The fraction of the deuterium atoms attached to the carbon adjacent to the

Scheme I



Scheme II



carbonyl was then determined by washing out these atoms with sodium methoxide and methanol, rechromatographing by vpc, and analyzing the resultant products for the remaining deuterium. Analysis of the *exo*-5-benzoylbicyclo[2.1.1]hexane obtained from the thermolysis of **9** indicated that it contained only 50% of the deuterium after the exchange, all of which was located in the 6-anti position. The Δ^2-cyclopentenylacetophenone, isolated from the thermolysis of **9**, also retained only 50% of the deuterium after the exchange. Its nmr showed that the deuterium was incorporated into the vinyl region (25% reduction in peak integration). These observations provide strong support for the thermal cleavage and 1,5-H transfer mechanism outlined above (see Scheme II).

Tricycloheptanol **6** was found to be extremely sensitive to basic conditions. When treated with base, **6** undergoes rapid cleavage to *exo*-5-benzoylbicyclo-[2.1.1]hexane (**4**) (85%). The base induced fragmentation of **6** is another example of an SEl reaction with carbon as the leaving group.[49] The elegant studies of Cram and coworkers have shown that the stereochemistry of the SEl reaction depends on the nature of the solvent.[49] Retention of configuration predominates in solvents of low dielectric constant like *tert*-butyl al-

(43) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 125.
(44) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 188.
(45) K. B. Wiberg and D. S. Connor, *J. Amer. Chem. Soc.*, 88, 4437 (1966).
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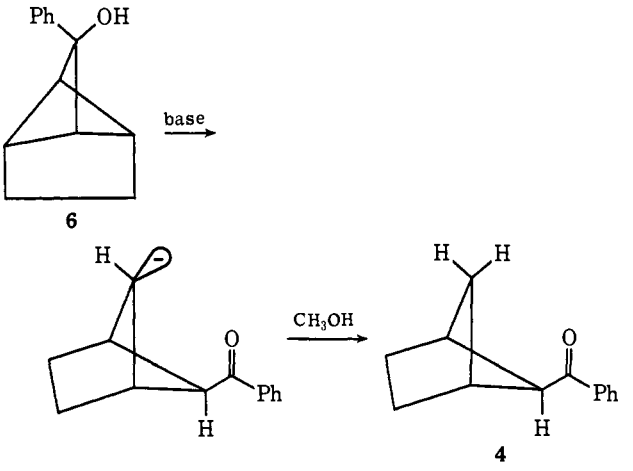
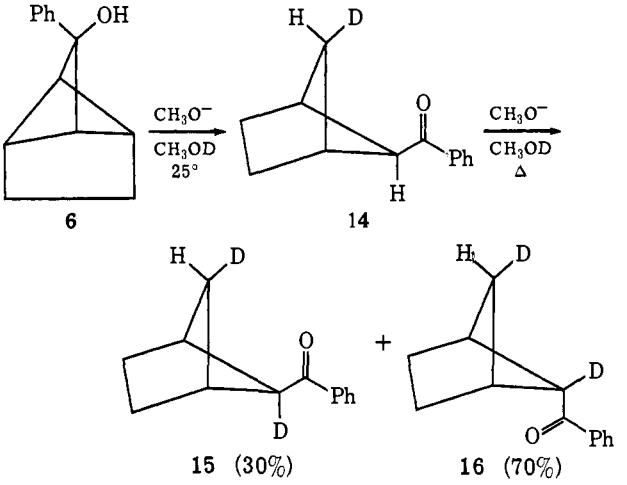


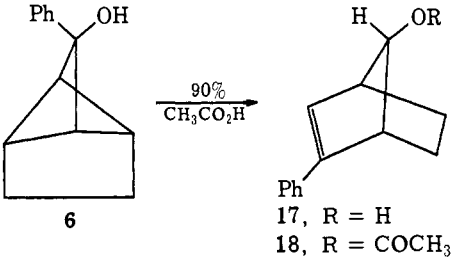


cohol, while inversion is the major course in solvents which have high dielectric constants and are good proton donors like methanol. The above reaction is very similar to the base-catalyzed ring opening of cyclopropanols[50] and consequently the mechanism of this cleavage became of prime interest. The solvent dependence of the stereochemistry of electrophilic attack at carbon has been studied in the base-catalyzed cleavage of cyclopropanols. In a dilute basic, ethanolic solution, *trans*-2-phenyl-1-methylcyclopropanol is isomerized to 4-phenyl-2-butanone.[51] The reaction has been shown to proceed *via* inversion of configuration. Nickon has shown that nortricyclanol undergoes base-catalyzed reketonization to norbornanone with 90% net inversion, independent of solvent.[52]

In order to obtain additional information about the transition state involved in the base-catalyzed ring opening of **6**, we have examined the stereochemistry of the base-catalyzed conversion of **6** to **4**. The base-catalyzed opening of **6** was carried out in methanol-*d* at 25° using sodium methoxide as the base. Under these conditions the reaction was complete in 0.5 hr, and the sole product was *exo*-5-benzoylbicyclo[2.1.1]-hexane. Under the reaction conditions used there was negligible isomerization of the exo ketone to the thermodynamically more stable endo ketone. Nmr and mass spectral analysis of the pure ketone (**14**) isolated showed that it was monodeuterated. The fact that the signal for the anti-6 hydrogen was a doublet (J = 7.0 Hz) at τ 9.02 and integrated for a full proton indicated that the reaction had occurred with >98% retention of configuration. When **14** was refluxed in methanol-*d* in the presence of sodium methoxide for 18 hr, a mixture of *exo*- (**15**) and *endo*- (**16**) 5-benzoylbicyclo[2.1.1]hexanes was obtained (ratio exo/endo = 1:2.3). The signal for the anti-6 hydrogen of the exo ketone (**15**) appeared as a singlet at τ 9.02. The signal for the anti-6 hydrogen of the endo ketone (**16**) also appeared as a singlet at τ 9.21.

The extensive studies of Cram have shown that SEl reactions give predominantly inversion in solvents of high dissociating power capable of donating protons.[49] This was interpreted to be a result of shielding of the front side of the carbanion by the leaving group and of rapid protonation of the carbanion by the solvent. By analogy, inversion would be expected in our system since the solvent (methanol) is highly proton donating and the conditions are extremely mild. The finding that the base-catalyzed cleavage of **6** to give **14** proceeds with >98% retention of configuration in methanol is exactly opposite to that expected. Although this result is unusual, it is not unprecedented. There are several examples in the literature which show that when the carbon leaving group remains in the same molecule as the carbanion, structural effects can be far more important than solvent effects in determining the stereochemical course of the reaction.[53–55] One possibility to account for the high degree of retention observed is that the departing carbonyl group distinguishes between the polar and nonpolar sides of the carbanion. The polar side will aggregate more with the solvent and lower the energy of activation of protonation. An alternate explanation is that the cage structure of **6** excludes solvent from part of one face of the developing carbanion. Protonation of the carbanion from the rear to give inversion would then generate an ion pair which would be separated by a cavity of low dielectric constant. This would be energetically less favorable than protonation from the same side as the departing carbonyl group.

The tricycloheptanol **6** was also found to be extremely unstable to acidic conditions. Treatment of **6** with 90% acetic acid afforded a mixture of 2-phenyl-*anti*-7-norbornenol (**17**, 60%) and *anti*-7-acetoxy-2-phenyl-2-norbornene (**18**, 40%). The structure of



alcohol **17** (*p*-nitrobenzoate derivative, mp 126–127°) is inferred from its composition and spectral data (see Experimental Section) and was unambiguously estab-

(50) C. H. Depuy, *Accounts Chem. Res.*, **1**, 33 (1968).
(51) C. H. Depuy, F. W. Breitbeil, and K. R. DeBrium, *J. Amer. Chem. Soc.*, 88, 3347 (1966).
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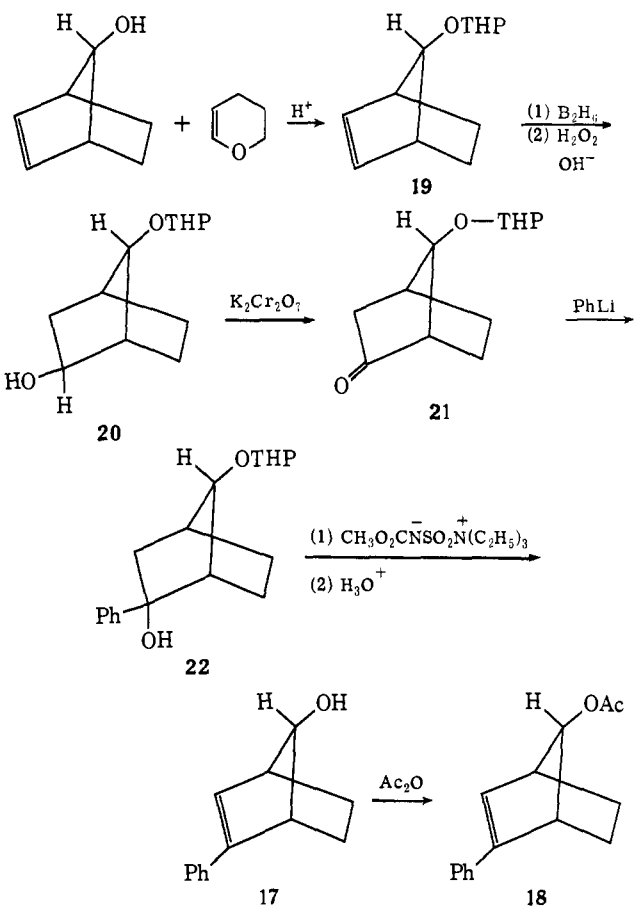
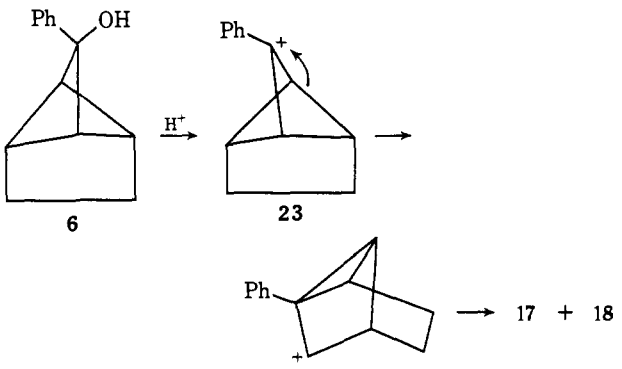
(55) W. T. Borden, V. Varma, M. Cabell, and T. Ravindranathan, *ibid.*, **93**, 3800 (1971).

lished by an independent synthesis. Treatment of *anti*-7-norbornenol with dihydropyran in the presence of acid gave *anti*-7-norbornenyl tetrahydropyranyl ether (**19**) which was hydroborated using standard conditions to give *anti*-7-tetrahydropyranyl-*exo*-norbornan-2-ol (**20**). Oxidation of **20** to ketone **21** followed by reaction with phenyllithium afforded *anti*-7-tetrahydropyranyl-2-*exo*-phenylnorbornan-2-ol (**22**). The tertiary alcohol was dehydrated using methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt according to the procedure of Burgess, Penton, and Taylor.[56] This was followed by removal of the protecting group by treatment with concentrated acid. The sample of **17** produced by this route was identical with the alcohol obtained from the reaction of **6** with 90% acetic acid. These syntheses are summarized in Scheme III. The structure of acetate **18** was established by the reaction of **17** with acetic anhydride.

Scheme III



The facile rearrangement encountered with **6** points to the exceptional reactivity of the tricyclo[3.2.0.0^{2,6}]-7-heptyl cation and the high propensity for it to undergo bond reorganization. The products formed can best be rationalized in terms of a tricyclo[3.2.0.0^{2,6}]hept-7-yl cation intermediate (**23**) which undergoes subsequent reorganization by C–C migration to the tricyclo-[3.2.0.0^{2,7}]hept-6-yl (**24**) cation system. The propensity of the tricyclo[3.2.0.0^{2,7}]hept-6-yl cation to undergo rearrangement to the *anti*-7-norbornenyl system is well documented in the literature.[57-61] Precedence for the



rearrangement of cation **23** to **24** is found in earlier work in our laboratory dealing with the acid-catalyzed rearrangement of the 2-phenylbicyclo[1.1.1]pentan-2-ol system.[62]

Discussion of the mechanistic details of the photoreaction of **4** as well as the photochemistry of the epimeric *endo*-5-benzoylbicyclo[2.1.1]hexane system will be presented in the following article.

Experimental Section[63]

Bicyclo[2.1.1]hexane-*exo*-5-carboxylic acid was prepared according to the procedure of Meinwald and coworkers:[40] mp 51–52° (lit.[40] 51–52°).

***exo*-5-Benzoylbicyclo[2.1.1]hexane (4).** Bicyclo[2.1.1]hexane-*exo*-5-carboxylic acid (1.0 g) was dissolved in 30 ml of anhydrous ether in a three-necked flask equipped with a magnetic stirrer, reflux condensor, and pressure-compensated dropping funnel. Phenyllithium (9.0 ml of a 2.2 *M* solution) was added over a period of 1 hr at a rate so as to maintain a steady reflux. The mixture was stirred for an additional 0.5 hr and then hydrolyzed by the addition of a saturated ammonium chloride solution. When two clear layers had formed, the ether layer was separated, washed with saturated sodium carbonate solution and twice with water, and dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* left a colorless liquid which solidified on standing. Vacuum sublimation of the crude solid (1.2 g) at 45° (0.1 mm) in a microsublimation apparatus gave crystals, mp 58–59° (74%), which gave a satisfactory elemental analysis for *exo*-5-benzoylbicyclo-[2.1.1]hexane (**4**).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.54. Found: C, 83.64; H, 7.40.

The infrared spectrum shows a strong carbonyl band at 5.98 μ and a series of sharp bands at 6.20, 6.91, 7.35, 8.15, 13.05, and 14.31 μ. The ultraviolet spectrum in 95% ethanol has maxima at 245 (ϵ 12,500) and 320 mμ (86). The nmr is in excellent agreement with the structure and has a triplet centered at τ 9.02 (1 H, J = 7.0 Hz), a broad singlet at τ 8.16 (5 H), multiplets at τ 7.78 (1 H), 7.06 (2 H), 2.50 (3 H), and 2.20 (2 H). The stereochemistry of the ketone is clear from its nmr spectrum, which shows a 7.0-Hz long-range coupling constant between the distant endo C-5 and C-6 protons.[41] Deuterated *exo*-5-benzoylbicyclo[2.1.1]hexane-5-*endo*-*d* (**8**) was prepared by treating the corresponding deuterated carboxylic acid with phenyllithium.[64] The nmr of monodeuterated ketone **8**

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(61) J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, **91**, 1548 (1969).
(62) A. Padwa and E. Alexander, *ibid.*, **92**, 5674 (1970).
(63) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra at 60 MHz were determined with the Varian Associates high-resolution spectrometer and at 100 MHz using a Jeolco-MH-100 spectrometer.
(64) *exo*-5-Chlorobicyclo[2.1.1]hexane-*exo*-6-carboxylic-6-*endo*-*d* acid was prepared from the irradiation of *syn*-7-chlorodiazonorcamphor in D_2O, according to the procedure of Meinwald, *et al.*[40] The chlorine substituent in the 5 position was removed by treatment of the acid with lithium in *tert*-butyl alcohol.

showed a doublet at τ 9.02 (J = 7.0 Hz) for the anti C-6 proton. The mass spectrum of **4** exhibited peaks with m/e 186 (M^+), 158, 120, 105 (base peak), and 77.

Photolysis of *exo*-5-Benzoylbicyclo[2.1.1]hexane in Benzene. A solution of 0.5 g of *exo*-5-benzoylbicyclo[2.1.1]hexane in 400 ml of benzene was irradiated at room temperature in a nitrogen atmosphere with a Hanovia 450-W mercury arc lamp using a Pyrex filter to eliminate wavelengths below 280 mμ. The progress of the reaction was followed by vapor-phase chromatography with a 8 ft × 0.25 in. aluminum column packed with 5% Degs on Chromosorb W at a flow rate of 60 cc/min and at a temperature of 150°; after 2 hr of irradiation the reaction was 90% complete. The solvent was removed on a rotatory evaporator and the remaining oil was subjected to preparative vpc. The chromatogram showed three peaks with retention times of 8.5, 9.8, and 11.5 min. The first peak to be eluted was identified as recovered starting material (10%). The second material to be eluted was identified as Δ^2-cyclopentenylacetophenone (**5**) (79%): bp 87–90° (0.5 mm); infrared spectrum, 5.98, 6.21, 6.90, 7.91, 8.23, 9.91, 10.25 μ; ultraviolet spectrum (95% ethanol) 248 (ϵ 11,700), 270 (600), and 305 mμ (75); nmr (CCl_4) multiplets at τ 8.75 (2 H), 7.73 (2 H), 7.15 (2 H), 6.90 (1 H), 4.35 (2 H), 2.65 (3 H), and 2.18 (2 H); mass spectrum (m/e) 186 (M^+), 120, 105 (base), 91, and 77.

The structure of this material was further confirmed by its unequivocal synthesis from Δ^2-cyclopentenylacetic acid and phenyllithium. The conversion of 5 g of Δ^2-cyclopentenylacetic acid to the phenyl ketone using phenyllithium (45 ml of a 2.20 M solution) in 150 ml of anhydrous ether was carried out exactly as described above for *exo*-5-benzoylbicyclo[2.1.1]hexane. The product, 4.6 g, was obtained as a colorless liquid: bp 90° (0.5 mm). The semicarbazone derivative had mp 186–187°.

Anal. Calcd for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04. Found: C, 68.93; H, 7.16.

The infrared and nmr spectra of Δ^2-cyclopentenylacetophenone prepared in this fashion were identical in every detail with those of the material isolated from the photolysis of *exo*-5-benzoylbicyclo[2.1.1]hexane.

7-Phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol (6). The third product collected from preparative vpc was a colorless liquid (11%) whose structure is assigned on the basis of the analytical and spectroscopic data cited. A urethane derivative was prepared by treating the tricyclic alcohol with *p*-bromophenyl isocyanate: mp 137–138°.

Anal. Calcd for $C_{20}H_{18}NO_2Br$: C, 62.51; H, 4.72. Found: C, 62.64; H, 5.12.

The infrared spectrum shows hydroxyl bands at 2.86 and 3.04 μ and a carbon–oxygen stretching band at 8.32 μ as well as bands at 9.05, 9.51, 9.79, 10.35, 10.61, 10.95, and 11.58 μ. The ultraviolet spectrum showed maxima at 248, 252, 258, and 265 mμ (ϵ 120, 170, 200, 160) characteristic of an isolated benzene ring. The mass spectrum shows the parent ion at m/e 186 and has major peaks at m/e 168, 120, 105, 91, and 77. The 100-MHz nmr spectrum showed the aromatic hydrogens as a singlet at τ 2.75, the two bridgehead hydrogens as a singlet at τ 7.34, a doublet at τ 6.55 (J = 7.0 Hz), a doublet at τ 7.88 (J = 7.0 Hz), the hydroxyl proton as a broad singlet at τ 7.09 (washed out with D_2O), and the four methylenic hydrogens as an AB quartet (J = 10.0 Hz) centered at τ 8.31. The nmr spectrum of 7-phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol-*d* (**9**) showed a coupling constant of 2.70 Hz (triplet) between the deuterium and the bridgehead hydrogen (1 bridgehead proton).

Irradiation of Δ^2-Cyclopentenylacetophenone. A solution of 0.5 g of Δ^2-cyclopentenylacetophenone (**5**) in 400 ml of benzene was photolyzed for 4 hr in the same manner as described above for *exo*-5-benzoylbicyclo[2.1.1.]hexane. Gas chromatographic analysis of the product mixture revealed the presence of acetophenone (63%), cyclopentadiene, starting material (10%), and a fourth component. The authenticity of the first three components was derived by comparison of vpc retention times on two columns, infrared spectra, and nmr spectra. The fourth peak consisted of a single component in low yield (5%) whose structure is assigned as 6-phenylbicyclo[3.2.0]hept-2-en-6-ol (**7**). The unsaturated alcohol had an infrared spectrum with bands at 2.79, 3.01, 6.02, 9.41, and 11.10 μ. The mass spectrum of this material included peaks with m/e 186 (M^+), 168, 167, 120 (base), 105, 91, and 77. The 100-MHz nmr spectrum shows a five-proton multiplet centered at τ 2.80, a singlet for the vinyl protons at τ 4.16 (2 H), a six-proton multiplet between τ 6.80–8.05, and the hydroxyl proton at τ 8.11.

Base-Catalyzed Epimerization of *exo*- and *endo*-5-Benzoylbicyclo[2.1.1]hexane. A 100-mg sample of *exo*-5-benzoylbicyclo[2.1.1]-hexane and 0.03 g of sodium methoxide in 10 ml of methanol was refluxed for 24 hr. To the resulting mixture was added 15 ml of water and the methanol was removed under reduced pressure. The aqueous layer was extracted with ether and the ethereal extracts were dried over sodium sulfate. Removal of the solvent and analysis of the residue by nmr spectroscopy showed that the ratio of exo to endo ketone was 1:23. The same ratio of isomers was obtained by treating *endo*-5-benzoylbicyclo[2.1.1]hexane with sodium methoxide in methanol.

Thermolysis of 7-Phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol (6). Thermal reactions were carried out in 25-ml Pyrex tubes that had been thoroughly cleansed and dried in an oven. A Neslab Instruments constant temperature apparatus was used for the thermolysis. In a typical run, 0.02 g of tricyclic alcohol **6** in 10 ml of benzene was heated in a sealed tube at 200° for 5 hr. The solvent was removed under reduced pressure and the residual oil was analyzed by vapor-phase chromatography using an 8 ft × 0.25 in. 10% DEGS on Chromosorb W at a temperature of 150°. The chromatogram showed two peaks which were subsequently identified as *exo*-5-benzoylbicyclo[2.1.1]hexane (30%) and Δ^2-cyclopentenylacetophenone (70%) by comparison with authentic samples.

The thermolysis of 7-phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol-5-*d* (**9**) was also investigated. In a typical experiment, 0.06 g of **9** in 10 ml of benzene was heated at 200° for 5 hr in a sealed evacuated tube. After thermolysis, the solvent was removed under reduced pressure and the crude residue was dissolved in 10 ml of a 5% sodium methoxide–methanol solution. The mixture was allowed to reflux for 24 hr and then the methanol was removed under reduced pressure and the resulting oil was washed with water and then extracted with methylene chloride. Evaporation of the methylene chloride afforded an oil which was subjected to preparative vpc. The products isolated were analyzed for their total deuterium content by nmr and mass spectroscopy. The *exo*- and *endo*-5-benzoylbicyclo[2.1.1]hexanes formed (combined yield 30% ratio exo:endo = 1:2.3) retained 50% of deuterium after refluxing in the protic medium. The Δ^2-cyclopentenylacetophenone (70%) formed also retained 50% of deuterium after exchange. Control experiments using a sodium methoxide–methanol-*d* solvent system indicated that only the acidic α proton(s) of **4** (or **5**) was exchanged under these conditions. Nmr integration of the mixture of exo and endo ketones showed that all the deuterium incorporated was located in the 6-anti position, *i.e.*, triplet at τ 9.02 and a doublet at τ 9.20, (total integration, 0.5 H). Nmr integration of the vinyl protons of Δ^2-cyclopentenylacetophenone showed that deuterium was incorporated into the vinyl region (singlet at τ 4.35, 25% reduction in peak integration).

Treatment of 7-Phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol with Sodium Methoxide in Methanol-*d*. A 0.05-g sample of tricyclic alcohol **6** was dissolved in 10 ml of methanol-*d*. To the above solution was added 5 ml of a 0.1% sodium methoxide–methanol-*d* solution. The mixture was allowed to stir for 0.5 hr.[65] The solvent was subsequently removed under reduced pressure and the residual oil obtained was dissolved in 10 ml of carbon tetrachloride, washed with D_2O, dried over magnesium sulfate, and concentrated under reduced pressure. Vapor-phase chromatography revealed the presence of only *exo*-5-benzoylbicyclo[2.1.1]hexane (85%). Nmr and mass spectral analysis of the ketone isolated showed that it was monodeuterated. The fact that the signal for the anti-6 hydrogen was a doublet at τ 9.02 (J = 7.0 Hz) and integrated for a full proton showed that the reaction had occurred with >98% retention of configuration. When the monodeuterated ketone was exchanged with 5 ml of a 5% sodium methoxide–methanol-*d* solution, the signal for the *anti*-6 hydrogen of the exo ketone became a singlet at τ 9.02 while the signal for the *anti*-6 hydrogen of the endo ketone was found as a singlet at τ 9.21.

Treatment of 7-Phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol with 90% Acetic Acid. A 0.2-g sample of **6** was added to 5 ml of 90% acetic acid and the resulting solution was allowed to stir for 4 hr at room temperature. The acetic acid was removed at 25° under reduced pressure and the remaining oil was subjected to preparative vpc using a 5% Degs on Chromosorb W column at 180°. The chromatogram showed two peaks with retention time of 10.8 and 18.2 min. The first peak to be eluted was identified as *anti*-7-acetoxy-2-phenyl-2-norbornene (**18**) (40%): infrared spectrum, 3.45, 5.75, 8.05, and 9.51 μ; mass spectrum (m/e) 228 (M^+), 168 (base), 158, 157, 155, 135, 115, 105, 91, and 77; nmr (60 MHz, $CDCl_3$) multiplets at τ 8.2–9.15 (4 H), singlet at τ 8.07 (3 H), multiplets at τ 7.13 (1 H), 6.79 (1 H), and 5.61 (1 H), doublet of doublets at τ 3.83

(65) Under these conditions there was negligible base epimerization of exo to endo bicyclic ketone.

(1 H, J = 3.5 and 1.0 Hz), and multiplet at τ 2.80 (5 H). The second product collected from preparative vpc was identified as 2-phenyl-*anti*-7-norbornenol (**17**) (60%) on the basis of the following evidence: bp 70–72° (0.5 mm).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.89; H, 7.61.

The infrared spectrum shows a strong hydroxyl band at 3.0 μ and has other bands at 3.45, 6.20, 6.71, 6.91, 8.91, 9.29, 10.95, 11.31, and 11.94 μ. The ultraviolet spectrum (95% ethanol) had a λ_{max} at 261 nm (ϵ 12,000). The nmr shows a series of multiplets centered at τ 8.90 (2 H), 8.10 (2 H), 7.40 (1 H), 7.05 (1 H), and 6.40 (1 H), a singlet at τ 6.55 (1 H, disappears on addition of D_2O), a doublet of doublets at τ 3.95 (J = 3.5 and 1.0 Hz), and a five-proton multiplet for the aromatic protons at τ 2.90. The mass spectrum of **17** exhibited peaks with *m/e* 186 (M^+, base), 168, 157, 155, 129, 115, 105, 91, and 77. The *p*-nitrobenzoate derivative had mp 126–127°.

Anal. Calcd for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11. Found: C, 71.73; H, 5.16.

2-Phenyl-*anti*-7-norbornenol (**17**) could be converted to *anti*-7-acetoxy-2-phenyl-2-norbornene (**18**) by reaction with acetic anhydride in the presence of pyridine. A 0.05-g sample of **17** in 5 ml of benzene was added to 1.2 ml of anhydrous pyridine. The solution was stirred at room temperature while 0.5 ml of acetic anhydride was added. The solution was allowed to reflux for 1 hr and then stirred for an additional 12 hr at room temperature. The solution was diluted with 20 ml of water, extracted with ether, washed with 5% hydrochloric acid, and dried over sodium sulfate. Evaporation of the solvent gave 0.52 g of *anti*-7-acetoxy-2-phenyl-2-norbornene. The spectral properties of this compound were identical in every way with those of the acetate isolated from preparative vpc. The structure of this material was unambiguously established by comparison with an authentic sample synthesized in the manner described below.

Establishment of the Structure of *anti*-7-Acetoxy-2-phenyl-2-norbornene. Concentrated hydrochloric acid (10 drops) was added to a solution of 12 g of *anti*-7-norbornenol[66] in 12 ml of dihydropyran with vigorous shaking. Stirring was continued for 15 min and then 2 g of sodium hydroxide was added. Distillation to the crude reaction mixture gave 15 g (71%) of *anti*-7-norbornenyl tetrahydropyranyl ether (**19**): bp 55° (0.5 mm); infrared spectrum, 3.42, 7.50, 8.90, 9.35, 9.75, and 10.31 μ, nmr (60 MHz, $CDCl_3$) doublet at τ 9.1 (J = 6 Hz, 2 H), multiplets at τ 8.45 (9 H), 7.50 (2 H), 6.50 (2 H), and 5.62 (1 H), and triplet at τ 4.25 (2 H), J = 3.0 Hz).

To 10 g of the above ether in 150 ml of anhydrous ether was added 15 ml of 2 *M* diborane solution. The mixture was allowed to stir for 1 hr and then was diluted with water (20 ml), followed by the addition of 20 ml of a 30% hydrogen peroxide solution and 20 ml of a 3 *N* sodium methoxide solution. After stirring for an additional 1 hr, the mixture was extracted with ether and the ethereal extracts were washed with water and dried over sodium sulfate. Evaporation of the solvent gave 10.7 g (98%) of *anti*-7-tetrahydropyranyl-*exo*-norbornan-2-ol (**20**): bp 62° (0.5 mm); ir, 3.00, 3.42, 7.39, 8.90, 9.35, 9.75, and 10.30 μ; nmr (60 MHz, $CDCl_3$) τ 8.87 (1 H, t, J = 7.0 Hz), τ 8.40 (13 H, m), τ 6.50 (4 H, m), τ 5.5 (1 H, m), τ 5.23 (1 H, m).

The colorless alcohol **20** (5 g) was dissolved in 25 ml of acetone and to the solution was added a 2.65 *M* potassium dichromate solution until the orange-red color persisted. The reaction mixture was extracted with ether, and the ethereal extracts were washed several times with water and dried over sodium sulfate. Evaporation of the ether gave 4.0 g of *anti*-7-tetrahydropyranyl-2-norbornanone (**21**) (80%) as a clear oil: ir 3.43, 5.71, 8.86, 9.30, 9.62, and 10.31 μ; nmr (60 MHz, $CDCl_3$) multiplets τ 7.5–9.2 (13 H), 4.35 (4 H), and 5.5 (1 H).

The conversion of 1 g of **21** to *anti*-7-tetrahydropyranyl-2-*exo*-phenylnorbornan-2-ol (**22**) was carried out using 2.5 ml of a 2.2 *M* phenyllithium solution to give 1.1 g (82%) of a liquid, bp 60° (0.5 mm). The infrared spectrum showed bands at 2.96, 7.0, 8.93, 9.32, 9.65, 9.85, and 10.35 μ. The nmr spectrum (60 MHz) showed multiplets centered at λ 8.5 (12 H), 7.1 (1 H, disappears on D_2O addition), 6.5 (4 H), 5.55 (1 H), 5.25 (1 H), and 2.80 (5 H).

The dehydration of **22** was carried out using the procedure of Burgess, Penton, and Taylor.[56] A mixture of 2.0 g of *anti*-7-tetrahydropyranyl-2-*exo*-phenylnorbornan-2-ol (**22**) and 1.8 g of methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt in 25 ml of benzene was heated at reflux for 6 hr. The reaction mixture was then poured into 100 ml of water and stirred for 15 min. The benzene layer was dried and evaporated under reduced pressure. The resulting oil was taken up in 25 ml of 95% methanol and acidified with concentrated hydrochloric acid at 0°. After stirring for 15 min, the mixture was diluted with 200 ml of water and extracted with ether. The ether was dried over sodium sulfate and evaporated under reduced pressure. The crude oil was distilled at 70° (0.5 mm) to give 0.49 g (40%) of 2-phenyl-*anti*-7-norbornenol. The spectral properties of this compound were identical in every way with those of the alcohol isolated previously. Conversion of the synthetically prepared alcohol to the acetate in the manner previously described gave *anti*-7-acetoxy-2-phenyl-2-norbornene (**18**).

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