Optically Active 2-*endo*-Methyl-2-*exo*-norbornyl Acetate (5-OAc). A homogeneous sample of the *t-exo* alcohol, $[\alpha]_D$ +2.78° (chloroform), was acetylated with excess acetic anhydride and pyridine at 100° for 13 hr in the usual manner and distilled to give a 94% yield of acetate **5**-OAc, whose infrared spectrum and retention times on vpc were identical with those of authentic racemic material. Capillary vpc on columns L and N indicated 0.75% *t-endo* acetate **10**-OAc was present; rotations: $[\alpha]^{25}_D$ −1.01°; $[\alpha]^{25}_{365}$ −3.36° (*c* 5.2–5.4, chloroform). This acetate was reduced with lithium aluminum hydride in the usual manner to give alcohol **5**-OH with the same rotation as that of the starting material. Analysis by capillary vpc on column L indicated the absence of 1-methyl-2-*exo* alcohol **3**-OH where less than 0.05% could have been detected.

Optically Active 1-Methyl-2-*exo*-norbornyl Acetate (3-OAc). Following the method previously reported,[13] 6.08 g of *t-endo* alcohol **10**-OH, $[\alpha]_D$ −6.45° (chloroform), was solvolyzed in acetic acid–sulfuric acid for 1.0 hr at 98°. Under these conditions, a few per cent each of *t-exo* acetate **5**-OAc and *t-endo* acetate **10**-OAc were present in addition to **3**-OAc. Preparative vpc on column D using a Wilkens Autoprep 700A with automatic 60-μl injections converted the *t-exo* acetate **5**-OAc to olefins and cleanly separated the desired product **3**-OAc from the *t-endo* acetate **10**-OAc. Distillation of the purified acetate separated it from the eluted column packing and gave 4.08 g (52%) of material whose infrared spectrum and retention times on vpc were identical with those of authentic racemic material. Capillary vpc on column N indicated a total of less than 0.2% of impurities; rotations: $[\alpha]^{25}_D$ +9.29°; $[\alpha]^{25}_{365}$ +28.0° (*c* 5.2–5.4, chloroform).

Optically Active 1-Methyl-2-*exo*-norbornanol (3-OH). The above acetate, $[\alpha]_D$ +9.29°, 0.722 g (4.29 mmoles), was reduced with 0.16 g of lithium aluminum hydride in the usual manner. Complete sublimation of the crude residue yielded 0.47 g (87%) of colorless, crystalline alcohol **3**-OH. The infrared spectrum and retention times on vpc were identical with those of pure, racemic material prepared in a similar manner; rotation: $[\alpha]^{25}_D$ +0.21°; $[\alpha]^{25}_{365}$ −2.11° (*c* 5.8–5.9, chloroform).

The alcohol recovered from the rotations was converted to the acetate with excess pyridine and acetic anhydride at 100° for 24 hr to give product with a rotation identical with that of the starting material.

2-*endo*-Methyl-2,3-*cis*,*exo*-norbornanediol (14). A sample of 2-methyl-2-norbornene[37] (0.20 g) was dissolved in 25 ml of dry ether. A stirred solution of 0.50 g of osmium tetroxide in 25 ml of ether was cooled to 0°, protected by a drying tube, and the olefin solution was added dropwise from a pressure-equalizing dropping funnel. A black solid precipitated during the addition; afterwards the mixture was allowed to stir overnight at room temperature. The black osmate ester was collected by filtration and added to a reaction flask containing 5.0 g of sodium sulfite, 25 ml of ethanol, and 25 ml of water. After heating at reflux for 1 hr on the steam bath, this mixture was filtered, and the filtrates were concentrated to dryness at the aspirator. The solid residue was extracted nine times with methylene chloride, and the organic extracts were combined and dried over magnesium sulfate. After filtration, the solvent was evaporated at the aspirator, leaving a greenish oil which distilled bulb to bulb to give a waxy solid.

This material exhibited an intense, broad O–H band in the infrared as well as a small C=O band due to an unknown contaminant. The diol was characterized by its nmr, which showed a broad signal at δ 4.1 (2 H) assigned to the hydroxyl protons and a slightly broadened absorption at δ 1.3 (about 4 H). Superimposed on the δ 1.3 absorption was a sharp singlet due to the methyl group, deshielded by the *gem*-hydroxyl function.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.70; H, 9.82.

Rearrangement of 2-*endo*-Methyl-2,3-*cis*,*exo*-norbornanediol (14). A round-bottomed flask was charged with 4 ml of concentrated sulfuric acid and cooled to −8° in an ice–salt bath. The cold solution was stirred rapidly with a magnetic apparatus, and 0.040 g of the solid diol **14** was added and allowed to stir in the acid for 10 min. After this time the yellow reaction mixture was poured onto cracked ice and extracted three times with pentane. The pentane was washed four times with saturated brine and dried over sodium sulfate. Careful removal of the solvent left about 30 mg of material which showed only one peak on capillary vpc column N-1, identical in retention time with 3-*endo*-methyl-2-norbornanone (**15b**). Control experiments showed that (1) less than 0.03% of the *exo*-methyl epimer could have been detected, and (2) both epimeric ketones were stable under the reaction conditions.

(37) K. Alder and H. J. Ache, *Chem. Ber.*, **95**, 503, 511 (1962).

Studies on the Molecular Geometry of the Norbornyl Cation. I. The Synthesis and Acetolysis of the *exo*- and *endo*-4,5-*exo*-Trimethylene-2-norbornyl *p*-Toluenesulfonates

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Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received January 3, 1967*

Abstract: 4,5-*exo*-Trimethylene-2-norbornene (**10**) has been synthesized from a monosubstituted cyclopentadiene **9** using an intramolecular Diels–Alder reaction, and from this intermediate *exo*- and *endo*-4,5-*exo*-trimethylene-2-norbornyl *p*-toluenesulfonates (**11**, R = Ts, and **16**, R = Ts) have been prepared. These sulfonates undergo acetolysis (25°) at relative rates of 8.6:1. The ratio of rate constants (25°) for acetolysis of the *exo*-sulfonate **11**, R = Ts, and 2-*exo*-norbornyl *p*-toluenesulfonate is 1:85, whereas the corresponding ratio for the *endo*-sulfonate **16**, R = Ts, and 2-*endo*-norbornyl *p*-toluenesulfonate is 1:2.5. The depressed rate for the tricyclic *exo*-sulfonate **11**, R = Ts, relative to 2-*exo*-norbornyl *p*-toluenesulfonate is readily explained in terms of bridging of carbon in the transition state for ionization, but seems to be contrary to expectations based on ionization to a localized (classical) carbonium ion. Thus, the present results favor the *bridged-ion* mechanism for acetolysis of 2-*exo*-norbornyl arenesulfonates.

A large body of data relating to the solvolysis reactions of various bicyclo[2.2.1]heptanes holding leaving groups such as halide or arenesulfonate at C_2 is now available.[1,2] It is clear, especially from extensive investigations of the parent 2-norbornyl series, that these reactions exhibit characteristics which sharply differentiate them from simple aliphatic or monocyclic

(1) For an excellent recent review see G. D. Sargent, *Quart. Rev.* (London), 20, 301 (1966).

(2) A collection of reprints of key papers in this field along with an authoritative commentary has been provided by P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

analogs. These properties, due in large part to special features of the norbornyl cation,[3] include[1,4-9] (1) extraordinary ease of Wagner–Meerwein rearrangement of C_6 from C_1 to C_2 (as compared with other reaction paths); (2) dependence of reactivity on orientation at C_2, specifically, generally higher solvolysis rates for various 2-*exo* derivatives as compared with the corresponding 2-*endo* compounds; and (3) extraordinarily stereospecific formation of *exo*-substitution products starting from 2-*exo*-norbornyl derivatives. Similar behavior has been noted for a number of methyl-substituted norbornyl derivatives.[1,5] These distinctive characteristics of the norbornyl cation have been interpreted by some[1,4,5] in terms of a mechanism in which ionization is assisted by the rearrangement of C_6 from C_1 to C_2 to lead directly to an intermediate bridged ion **1** (*bridged-ion mechanism*), while others[10-12] have held to the view that the available data can be explained on the basis of rapidly rearranging localized norbornyl cations **2** (*classical-ion mechanism*). Additional evi-

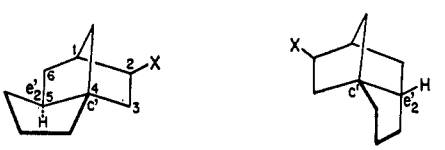
1 **2**

dence which can serve to exclude one of these alternatives is clearly desirable. One possible approach toward this end is the detection of positive charge at C_1 and/or C_6 in the transition state using kinetic measurements with substrates having electron-supplying groups at these centers. Although studies have been carried out along these lines,[1,13,14] they have not yielded the sort of results which allow an unambiguous decision between the two theories. Another way of distinguishing between bridged-ion and classical-ion mechanisms is made possible in principle by the fact that the transition states for these paths should involve different geometries of the ring system. This paper describes the first part of an investigation aimed at revealing more clearly the molecular geometry of the cationic species which intervene in the ionization reactions of 2-norbornyl *p*-toluenesulfonates. In general, a reasonable basis for such a test could be the introduction of a bridge (or a set of bridges) into the bicyclo[2.2.1]heptane system in such a way as to produce either a large *increase* or *decrease* in total strain for the ring system with migration of C_6 from C_1 to C_2 while at the same time preserving to a maximum extent for the initial and rearranged structures the exact geometry of the basic bicyclo[2.2.1]heptane part and also the exact environment of groups at the *exo* and *endo* orientations at C_2.

Before describing the specific molecular system which we have studied, a general consideration of the effect of Wagner–Meerwein rearrangement on the various positions of the norbornyl skeleton is appropriate. Let the various types of ring atoms in structure **3** be represented by descriptive letters as follows: common atoms 1 and 4 as *c* and *c'*, methano bridge as *m*, ethano bridge members as e_1, e_1' for the bridge bearing the leaving group, and e_2, e_2' for the other. After Wagner–Meerwein rearrangement of carbon, these atoms assume the locations indicated in **4**. It will be noted that only two atoms, *c'* and e_2', are both unchanged in type and

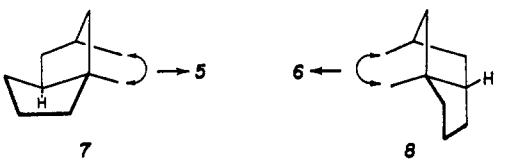
3 **4**

remote from the leaving and entering groups and also that *exo*- and *endo*-substituent interconversion occurs at e_2'. Therefore, if a chain of atoms is added to join *c'* and *exo*-e_2' in **3** with establishment of a new ring, the rearrangement **3** to **4** will produce a *stereoisomeric* system, in principle of different energy, without any essential interference with the environment of the leaving or entering groups. In the specific case of a trimethylene bridge, the stereoisomer $c'(CH_2)_3e_2'$(*exo*) (**5**) can be formed with only a minor amount of additional angle strain. In contrast, the stereoisomer $c'(CH_2)_3e_2'$(*endo*) (**6**) is formed with much angle strain in addition to the norbornyl strain. Crude estimates of



5 **6**

the difference in strain energy between **5** and **6** (principally angle strain) have been made in two different ways. In the first, the angle strain formula of Westheimer[15] has been used, taking into account only the distortions of C–C–C angles and using the values for ring angles as measured from (a) Cenco Peterson molecular models and (b) Fieser–Dreiding molecular models; this gave strain energy differences of (a) 7.2 kcal/mole and (b) 8.1 kcal/mole, with the likelihood that both estimates are too high[15] rather than too low. The second way for estimation of strain energy differences rests upon the recognition of **5** and **6** as derivatives of *cis*- and *trans*-pentalane, respectively. The ring systems of **5** and **6** can be formed by the joining of atoms in the hypothetical *cis*- and *trans*-pentalane derivatives **7** and **8**. Simulation of the ring closure of



7 **8**

(3) Unless otherwise indicated, the term norbornyl cation when used herein refers to the cation derived from heterolysis of appropriate 2-norbornyl derivatives.

(4) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **71**, 2953 (1949); **74**, 1147, 1154 (1952).

(5) S. Winstein, *et al.*, *ibid.*, **87**, 376, 378, 379, 381 (1965).

(6) S. Winstein, E. Vogelfanger, K. C. Pande, and H. F. Ebel, *ibid.*, **84**, 4993 (1962).

(7) H. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965).

(8) E. J. Corey, J. Casanova, P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963).

(9) S. Smith and J. P. Petrovitch, *Tetrahedron Letters*, 3363 (1964).

(10) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 140.

(11) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

(12) M. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966).

(13) D. C. Kleinfelter, *Dissertation Abstr.*, **22**, 428 (1961).

(14) D. C. Kleinfelter and P. von R. Schleyer quoted by J. A. Berson in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 182.

(15) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 533 *et seq.*

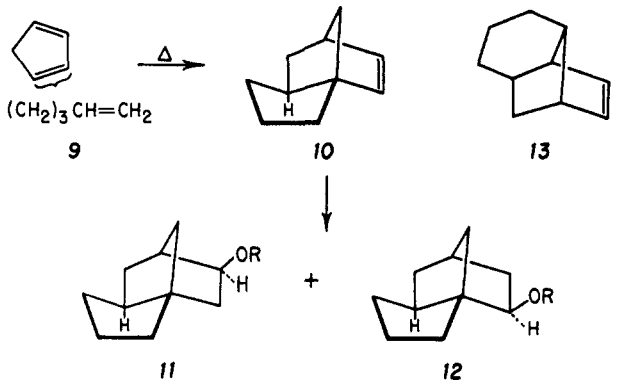


Figure 1.

7 and 8 with the above-named types of models indicates that the increase in angle strain upon ring closure is 10–20% greater with 7 than with 8, which probably amounts to a difference of 0.5–1 kcal/mole.[16] This would roughly be offset by changes in torsional strain from 7 and 8 to 5 and 6, and, therefore, it appears that the difference in strain energy between 5 and 6 should be approximately the same as for *cis*- and *trans*-pentalane systems, *i.e.*, *ca.* 6–7 kcal/mole.[17]

Thus, there can be little doubt that 5 is substantially less strained than the isomer 6. This is also obvious simply by inspection of models which reveals additionally that the process of Wagner–Meerwein rearrangement of 5 to 6 results in a steady increase in strain. Therefore, it would be expected that if ionization leads to *bridging* in the transition state for solvolysis of 2-*exo*-norbornyl *p*-toluenesulfonate, the *p*-toluenesulfonates corresponding to 5 and 6 should react more slowly and more rapidly, respectively. On the other hand, the solvolysis rates for the three *endo*-*p*-toluenesulfonates should all be approximately the same, since presumably there should be little or no bridging of C_6 in the transition state and also no other differences for the three cases (*e.g.*, steric acceleration or steric interference[10–12] to ionization should be the same). A reasonable prediction on the basis of the *classical-ion mechanism* is that the rates of solvolysis of the *exo*-*p*-toluenesulfonates 5 and 6 should be essentially the same as for the 2-*exo*-norbornyl case and, similarly, that the rates for the *endo*-*p*-toluenesulfonate isomers of 5 and 6 should be approximately the same as 2-*endo*-norbornyl.

It should be noted that the C_1–C_2–C_3 angle in 5 and 6 as observed in models appears to have the value which is normal for the simple bicyclo[2.2.1]heptane ring system (further evidence on this point appears in the following section). The number of carbons in the extra bridge connecting c' and e_2' in 5 and 6 appears to be optimal for the purposes of revealing the molecular geometry of the norbornyl cation; fewer carbons would introduce too much strain and perturbation of the bicyclo[2.2.1]heptane system in *both* the *exo*- and *endo*-bridged structures, whereas a larger number of bridge atoms (>3) would diminish the deferential strain between the *exo*- and *endo*-bridged structures to too small a value.

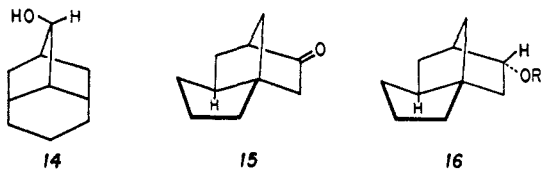
(16) A total closure strain energy from 7 and 8 to 5 and 6, respectively, is probably somewhat less than the strain energy of norcamphor (*ca.* 6 kcal/mole); see K. Alder and G. Stein, *Ber.*, 67, 613 (1934); G. Becker and W. A. Roth, *ibid.*, 67, 627 (1934); R. P. Linstead, *Ann. Rept.* (London), 32, 315 (1935).

(17) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 436 (1935); 611 (1936).

Synthetic Studies

The synthesis of 4,5-*exo*-trimethylene-2-*exo*-norbornyl *p*-toluenesulfonate was accomplished in four steps as outlined in Figure 1. Alkylation[18] of cyclopentadienylsodium by 5-bromo-1-pentene produced a mixture of monosubstituted cyclopentadienes 9 with the substituent principally at C_1 and C_2 as indicated by nmr measurements. When a dilute solution of the mixture of Δ^4-pentenylcyclopentadienes 9 was heated in tri-*n*-butylamine as solvent, 4,5-*exo*-trimethylene-2-norbornene (10) was produced in good yield.[19,20] The structure of the product from this reaction is indicated by physical, analytical, and chemical data. The alternative nonstereoisomeric internal Diels–Alder structure 13 could be excluded from consideration by the nmr spectrum of the product which exhibited a sextet consistent with the AB part of an ABX pattern centered at 6 ppm[21,22] due to two olefinic protons, a broad band due to a *single* bridgehead (and allylic) proton at 2.8 ppm,[23] and the remaining aliphatic protons (found 11.0) between 2.0 and 1.0 ppm. Structure 13 can also be excluded from the nmr spectra of various transformation products of 10, *e.g.*, the *exo*-2,3-oxide, and also on the basis of chemical data. The chemical evidence which excludes the structure stereoisomeric with 10 but having a 4,5-*endo*-trimethylene bridge will be presented below.

Hydroboration of 10 with disiamylborane[24,25] led to a mixture of the alcohols 11, R = H, and 12, R = H, in a ratio of 92:8. The same alcohols were also produced using diborane as the reagent for hydroboration, but the process was less useful for synthesis, since the products 11, R = H, and 12, R = H, were formed in a ratio of *ca.* 3:1; further, a third isomeric alcohol 14 was produced in certain runs evidently because of the use of more boron trifluoride than required for the generation of diborane reagent from sodium borohydride. The alcohol 11, R = H, was readily obtained from the 92:8 mixture *via* the crystalline 3,5-dinitrobenzoate ester. The crystalline alcohol so purified was converted to the crystalline *p*-toluenesulfonate 11, R =



Ts, mp 66.5–68°, by exposure to *p*-toluenesulfonyl chloride in pyridine. Oxidation of the alcohol 11,

(18) K. Alder and H. J. Ache, *Ber.*, 95, 503 (1962).

(19) See G. Brieger, *J. Am. Chem. Soc.*, 85, 3783 (1963).

(20) A small amount (*ca.* 5%) of a second isomeric product was also formed; this by-product will be dealt with in later papers.

(21) All nmr data cited in this paper refer to parts per million shift downfield from tetramethylsilane as internal reference.

(22) Reproductions of this and other spectra are available in the Ph.D. dissertation of R. S. Glass, Harvard University, 1966.

(23) For reference nmr data on norbornenes see (a) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, 86, 1171 (1964); (b) E. I Snyder and B. Franzus, *ibid.*, 86, 1166 (1964); (c) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji and H. Tanida, *Tetrahedron Letters*, 9 (1966).

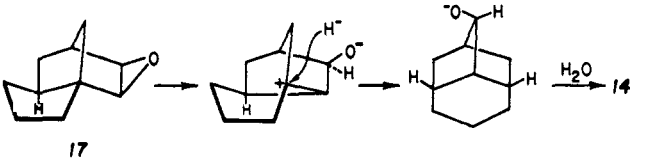
(24) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(25) G. Zweifel, N. R. Ayyangar, and H. C. Brown, *J. Am. Chem. Soc.*, 85, 2072 (1963), and references cited therein.

R = H, by chromic acid afforded the corresponding ketone **15** (carbonyl absorption 1749 cm^{-1}, 5.72 μ in CCl_4), which was reduced with sodium borohydride in methanol to yield the crystalline *endo* epimer of **11**, R = H (**16**, R = H). Reaction of **16**, R = H, with *p*-toluenesulfonyl chloride gave the corresponding *p*-toluenesulfonate **16**, R = Ts, mp 50–51.5°.

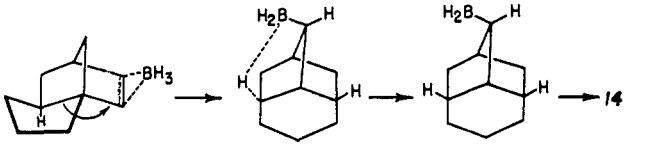
The nmr spectra[22] of the *exo* compounds **11**, R = H, and **11**, R = CH_3CO, exhibit ROCH< proton resonance as a doublet of doublets centered at 3.88 and 4.70 ppm, respectively, whereas the nmr spectra of the *endo* compounds **16**, R = H, and **16**, R = CH_3CO, show the ROCH< as much more complex multiplets at 4.23 and 4.98 ppm, respectively. Similarly, the *p*-toluenesulfonate **11**, R = Ts, exhibits a ROCH< peak as an overlapping doublet of doublets (pseudo-triplet) centered at 4.57 ppm, and the corresponding peak in **16**, R = Ts, is a broad, complex multiplet centered at 4.80 ppm. The more complex splitting observed with the derivatives of **16** as compared with those of **11** indicate additional coupling of *ca.* 3 cps and, therefore, the adjacency of a bridgehead proton. This places the alcoholic function at C_2 rather than C_3 and confirms the assignment which follows from the known orientational tendencies of disiamylborane in addition to unsymmetrically substituted olefins.[24,25] Hydroboration would also be expected to produce *exo* rather than *endo* alcohols, and this too is supported by the nmr data, since resonance for *exo*-ethano protons occurs at lower field than for *endo*-ethano protons in norbornane derivatives with characteristic differences in chemical shift of 0.3–0.6 ppm.[26–29] The *endo* configuration for **16**, R = H, also follows from the generation of this alcohol by borohydride reduction of the corresponding ketone **15**.

Epoxidation of the tricyclic olefin **10** with monoperphthalic acid in ether produced the *exo*-2,3-oxide **17** in good yield. The nmr spectrum of this substance was completely consistent with structure **17**. The protons attached to the epoxide ring give rise to a sharp doublet at 2.79 ppm and a broadened doublet at 2.96 ppm; a bridgehead hydrogen is responsible for a broad singlet at 2.42 ppm (*one proton only*), and a doublet at 0.7 ppm is clearly assignable to the 7-*anti* proton.[30] Reaction of the epoxide **17** with lithium aluminum hydride produced three isomeric alcohols, **11**, R = H, **12**, R = H, and **14** in a ratio of 33:63:4, whereas the use of lithium aluminum hydride–aluminum chloride produced only **11**, R = H, and **14** (ratio 24:76). The rearranged alcohol **14** must arise *via* a Wagner–Meerwein process which becomes more important than the competing process, SN2 attack by hydride, with the more acidic "mixed hydride"[31] as compared with lithium aluminum hydride. The rearrangement can be sketched (without regard for detail) as follows.



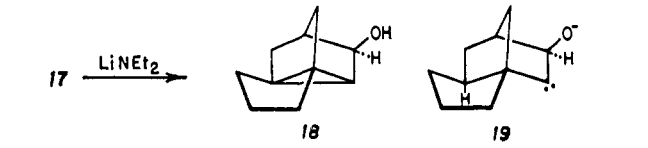
17

The occurrence of this rearrangement indicates clearly that the trimethylene bridge in **17** (and hence in **10**, etc.) must be *c'-exo-e₂'* and not *c'-endo-e₂'*. The structure of **14** follows from physical and chemical data, including oxidation to a ketone which must possess the oxo function at the methano bridge, since the carbonyl stretching band is found at 5.63 μ in the infrared.[32] The formation of **14** from the tricyclic olefin **10** by reaction with mixtures of diborane and boron trifluoride followed by oxidation with alkaline hydrogen peroxide is a most interesting reaction which is deserving of further study. At present we can only speculate as to mechanism; one possibility is a process such as the following in which boron trifluoride (not shown) is coordinated (hydrogen bond) to a borane hydrogen.[33] This rearrangement also requires that the starting



tricyclic olefin be formulated as 4,5-*exo*-trimethylene-2-norbornene (**10**) rather than the *endo* isomer. In fact, we have observed a whole series of such rearrangements which proceed with remarkable ease (even more readily than with the parent norbornyl system); some of these are outlined in a later section.

Independent evidence for the structure **10** as opposed to the *endo*-trimethylene formulation comes from the reaction of the oxide **17** with lithium diethylamide, which leads to a saturated tetracyclic alcohol which can be assigned structure **18** on the basis of physical and chemical data, much of which is discussed below. The mechanism of this reaction would appear to be analogous to other base-catalyzed rearrangements of 1,2-epoxides[34,35] which appear to proceed *via* β-alkoxy carbenes. The formation of **18** from such a carbene **19** appears only to be possible if the trimethylene bridge in the starting oxide **17** is *exo*.



17 **18** **19**

A number of experiments directed at the synthesis of 4,5-*endo*-trimethylene-2-norbornyl derivatives (**6**, X = *endo*- or *exo*-OH) have been carried out, but members of this series have not been obtained to date. Synthetic efforts to produce these compounds are continuing.

(26) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).
(27) E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).
(28) J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Am. Chem. Soc.*, **86**, 4074 (1964).
(29) P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2822 (1966).
(30) For the interesting basis of this assignment see (a) K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Letters*, 559 (1964); (b) K. Tori, K. Aono, K. Kitahonoki, R. Muneyuki, Y. Takano, H. Tanida, and T. Tsuji, *ibid.*, 2921 (1966). The observation of the characteristic 7-*anti*-proton peak in the oxide **17** also is inconsistent with structure **13** for the olefinic precursor.
(31) (a) E. L. Eliel, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **22**, 129 (1961); (b) E. C. Ashby and J. Prather, *J. Am. Chem. Soc.*, **88**, 729 (1966).
(32) (a) C. F. H. Allen, T. Davis, D. W. Stewart, and J. A. Van Allan, *J. Org. Chem.*, 20, 306 (1955); (b) C. F. H. Allen and J. A. Van Allan, *ibid.*, 20, 323 (1955); (c) C. J. Norton, Ph.D. Thesis, Harvard University, 1955; (d) P. Wilder and A. Winston, *J. Am. Chem. Soc.*, **78**, 868 (1956); (e) W. R. Hatchard and A. K. Schneider, *ibid.*, **79**, 6261 (1957); (f) D. E. Applequist and J. P. Klieman, *J. Org. Chem.*, **26**, 2178 (1961).
(33) Possibilities such as reaction *via* fluoroborane (BH_2F) or separate action of BF_3 and BH_3 also deserve consideration.
(34) A. C. Cope, M. Brown, and H. H. Lee, *J. Am. Chem. Soc.*, **80**, 2855 (1958).
(35) A. C. Cope, H. H. Lee, and H. E. Petree, *ibid.*, **80**, 2849 (1958).

Acetolysis Studies. Rates of acetolysis of 4,5-*exo*-trimethylene-2-*exo*-norbornyl *p*-toluenesulfonate (**11**, R = Ts) and 4,5-*exo*-trimethylene-2-*endo*-norbornyl *p*-toluenesulfonate (**16**, R = Ts) were measured at several temperatures in anhydrous acetic acid containing sodium acetate using the spectrophotometric method of Swain and Morgan,[36] which depends on the difference in intensity of absorption in the region 260–280 mμ between *p*-toluenesulfonate ion and *p*-toluenesulfonate esters. First-order kinetics were observed for both **11** and **16**, R = Ts, and the infinity readings were found to be stable. The kinetic results are summarized in Table I, which also presents data[37] on 2-*exo*- and 2-*endo*-norbornyl *p*-toluenesulfonates for comparison.

Table I. Kinetic Data for Acetolysis in Anhydrous Acetic Acid

p-Toluenesulfonate	Temp, °C	10^6k_1, sec^{-1}	Rel rate, 25°	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
4,5-*exo*-Trimethylene-2-*exo*-norbornyl (**11**, R = Ts)	90.65[a]	847		25.6	−2.6
	82.60[a]	382			
	67.68[a]	73.9			
	25.00[b]	0.283	3.4		
4,5-*exo*-Trimethylene-2-*endo*-norbornyl (**16**, R = Ts)	100.8[a]	371		26.7	−3.1
	85.16[a]	74.6			
	82.60[a]	55.8			
	25.00[b]	0.0328	0.4		
2-*exo*-Norbornyl	50.03[a]	480			
	25.00[c]	23.3	280	21.6	−7.2
2-*endo*-Norbornyl	100.4[c]	0.0675			
	25.00[c]	0.0828	1.0	25.8	−4.4

[a] These runs made with 0.010 *M* sodium acetate and <0.005 *M* substrate. [b] Calculated from data at other temperatures. [c] Taken from ref 37 (also calculated from data at other temperatures).

The ratio of acetolysis rate constants for the *exo*- and *endo*-tricyclic *p*-toluenesulfonates **11**, R = Ts, and **16**, R = Ts, is calculated as 8.6 at 25° and 6.8 at 82.6°; these are much smaller than the *exo*:*endo* ratio for the 2-norbornyl system, *e.g.*, 280 at 25°. The rate of acetolysis of the *exo*-tricyclic *p*-toluenesulfonate **11**, R = Ts, is much smaller than that for 2-*exo*-norbornyl, the relative rates at 25° being 1:82.5, respectively. In contrast, the acetolysis rates of the *endo*-tricyclic *p*-toluenesulfonate **16**, and 2-*endo*-norbornyl are very similar, the ratio at 25° being 1:2.5, respectively.

The lower rate of acetolysis of 4,5-*exo*-trimethylene 2-*exo*-*p*-toluenesulfonate (**11**, R = Ts) as compared with 2-*exo*-norbornyl might, for some obscure reason, be due to a difference in the tendency of the corresponding ion pairs to suffer acetolysis relative to internal return rather than to a difference in rates of ionization. This would seem unlikely *a priori*, but it also seems inappropriate because of data which have been obtained on the effect of added inert salt on the acetolysis of **11**, R = Ts. The acetolysis rate constants observed for **11**, R = Ts, in glacial acetic acid containing 0.01 *M* sodium acetate at 67.88° and varying molar concentrations of lithium perchlorate are: 76 (10^{-6}) at 0.00 *M* $LiClO_4$, 89.4 (10^{-6}) at 0.0098 *M* $LiClO_4$, 180 (10^{-6}) at 0.05 *M* $LiClO_4$, and 320 (10^{-6}) at 0.100 *M* $LiClO_4$. The evidence from other systems would tend to argue that as the concentration of $LiClO_4$ is increased to *ca.* 0.015 *M*, most of the internal return which can be prevented at all by this salt has been nullified (presumably this is return from "solvent-separated" ion pairs).[38-40] Under these conditions the rate of acetolysis of **11**, R = Ts, is still very much less than that of 2-*exo*-norbornyl. Further, the type of salt effect noted for the acetolysis of **11**, R = Ts, does not appear to provide any basis for supposing an abnormal reluctance for "solvent-separated ion pairs"[38-40] to react with solvent. It should also be noted that an argument can be given[40] that acetolysis of 2-*exo*-norbornyl *p*-bromobenzenesulfonate probably does not occur directly from the "intimate ion pair," *i.e.*, from the type of ion pair which is not subject to anion exchange with perchlorate. If such acetolysis could occur with 2-*exo*-norbornyl but not with the *exo*-tricyclic analog **11**, R = Ts, the lower rate of the latter might conceivably be rationalized (quite unconvincingly) along such lines.

The major product from acetolysis of the tricyclic *exo*-*p*-toluenesulfonate **11**, R = Ts, and the tricyclic *endo*-*p*-toluenesulfonate **16**, R = Ts, was in each case the tricyclic *exo*-acetate **11**, R = CH_3CO, which was formed to the extent of 91.5 and 92% of the total mixture of products, respectively. At least two more acetates were detected along with the major product from both **11**, R = Ts, and **16**, R = Ts; in each case these constituted *ca.* 4% of the total mixture. These were not identified due to the difficulty of separation from each other and from **11**, R = CH_3CO.[41] The vpc analyses indicated that one of the minor acetates could be the tricyclic *endo*-acetate **16**, R = CH_3CO, on the basis of correspondence of retention times. However, additional investigation of this possibility is required and is planned. Two hydrocarbons were also formed in the acetolysis of **11**, R = Ts, and **16**, R = Ts, in a total yield of *ca.* 4%. The preponderant hydrocarbon exhibited the same vpc behavior as the tricyclic olefin **10**.

Discussion

The results of this study are most simply interpreted in terms of the *bridged-ion mechanism* for the acetolysis of 2-*exo*-norbornyl sulfonates. This mechanism should lose much or all of its driving force in the case of the tricyclic *exo*-*p*-toluenesulfonate, **11**, R = Ts (see introductory section), and so the slow acetolysis of this substrate relative to norbornyl is readily explained (and, in fact, was to be expected). In comparison, but also as predicted on the basis of the Winstein–Trifan arguments, 2-*endo*-norbornyl *p*-toluenesulfonate and the tricyclic *endo*-*p*-toluenesulfonate **16**, R = Ts, for which bridging is not to be expected in the transition state for ionization on stereochemical grounds, show quite similar reactivity. Here it should be noted that the carbonyl stretching frequencies for 4,5-*exo*-trimethylenenorcamphor (**15**) and norcamphor, measured under the same conditions (CCl_4 solution) with a Cary-White Model 90 infrared spectrometer (with polystyrene for calibration), were found to be 1749 and 1750 cm^{-1}, respectively. This would indicate

(36) C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).
(37) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965).
(38) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763, 2767 (1956).
(39) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *ibid.*, **78**, 328 (1956).
(40) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).
(41) Even the analytical resolution of the minor acetates from **11**, R = CH_3CO, was extremely difficult and could only be accomplished by the use of vapor phase chromatography (vpc) with a long capillary column.

that differences in angle strain at C_2 cannot be responsible for the different acetolysis rates observed in the *exo*-sulfonate series and also that the *endo*-sulfonate reactivities should be approximately the same.[42]

The *classical-ion mechanism*, in a straightforward interpretation, leads to the expectation that in acetolysis k(2-*exo*-norbornyl) $\cong$ k(**11**, R = Ts) and k(2-*endo*-norbornyl) $\cong$ k(**16**, R = Ts). This is *not* the case, and there does not seem to be any obvious reason for the depressed reactivity of the tricyclic *exo*-*p*-toluenesulfonate **11**, R = Ts, keeping in mind the data on the *endo* sulfonates. Substitution of simple alkyl at C_4 and/or C_5 would not be expected to produce a differential effect on the reactivities of **11** and **16**, R = Ts, in a *classical-ion mechanism*, especially since the effect of replacing hydrogen by methyl at these positions in the 2-norbornyl series is small either with regard to the *exo* rates alone or the *endo* rates alone.[1,43] The arguments which have been given in support of the *classical-ion mechanism*[10-12] include (1) greater steric hindrance to *endo* relative to *exo* group ionization to explain the observed relative solvolysis rates of *exo*- and *endo*-2-norbornyl derivatives and (2) some kind of steric effect which causes *endo* attack by solvent on the intermediate cation to be much slower than *exo* attack. There is little in these suggestions which helps to explain the results obtained in the present study.

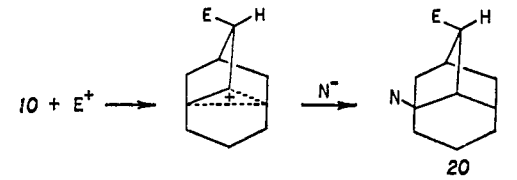
Thus we regard our results as providing clear support for the *bridged-ion mechanism* for solvolysis of 2-*exo*-norbornyl derivatives. However, it must be pointed out that confirmatory data from the study of the 4,5-*endo*-trimethylene-2-norbornyl sulfonates is highly desirable.

There is no evidence available at present which allows a clear assignment of mechanism for the acetolysis of the tricyclic *exo*-*p*-toluenesulfonate **11**, R = Ts. It is obviously possible that a part or even all of this reaction follows the classical pathway for ionization; again further study is in order.

The results reported here add further evidence that the bridged norbornyl cation is especially stabilized relative to the classical ion, but they provide no information as to the origin of that stabilization. One possibility deserves mention in this regard. Normally, *e.g.*, for aliphatic cations,[44] Wagner–Meerwein rearrangements proceed with low activation energies, perhaps on the order of a few kcal/mole. Assuming that the bridged ion which intervenes during such rearrangement has an energy very close to that of the transition state, it seems that only a small degree of extra stabilization (perhaps 3–7 kcal/mole) would be needed in certain systems to render the bridged ion more stable than a classical ion. At least part of this extra stabilization might be available in the bridged norbornyl cation from relief of angle strain. In the bicyclo[2.2.1]heptane nucleus a number of bond angles are distorted from normal values leading to considerable angle strain. The angles C_1–C_7–C_4 (*ca.* 95°), H–C_1–C_7, and H–C_4–C_7 (*ca.* 118°) are especially strained.[45] Much of this strain would be relieved in going to a symmetrically bridged ion with C_6–C_1 and C_6–C_2 distances *ca.* 1.70 A (*i.e.*, about 10% longer than a normal C–C single bond), and essentially all the strain would be relieved in a bridged structure with C_6–C_1 and C_6–C_2 distances of 1.8 A (only *ca.* 20% longer than normal for C–C).[46] Since the angle strain in the bicyclo[2.2.1]heptane ring appears to be *ca.* 6 kcal/mole,[16] it is clear that considerable stabilization is available to the symmetrically bridged ion through relief of angle strain. Of course other factors may also contribute to the end result. For example, "I strain"[47] might destabilize the classical cation (C_1–C_2–C_3 angle *ca.* 104°) substantially. Finally, as is well known, the geometry of 2-*exo*-norbornyl derivatives is ideal for migration of C_6 to C_2 during the ionization process.

The only data currently at hand for which the *bridged-ion mechanism* does not provide a ready and cogent explanation, in our view, are those on the acetolysis of 1-aryl-2-*endo*- and -2-*exo*-norbornyl *p*-toluenesulfonates.[48] Using the Hammett equation,[49] it was found that the data on *both exo* and *endo* sulfonates were correlated better using σ[49] constants rather than σ^+ values of Brown and Okamoto[50] and further that the ρ values for the 2-*exo*- and 2-*endo*-sulfonates were similar and low; at 25° ρ_{exo} = −1.36 and ρ_{endo} = *ca.* −1.14.[48] There may be simple explanations of these data; these are not apparent at present, however.

Reactions of 4,5-*exo*-Trimethylenebicyclo[2.2.1]heptane Derivatives. In this section we record certain transformations of the tricyclic olefin **10** and its 2,3-oxide **17** which are of interest in connection with the development of the chemistry of this interesting system and which also serve to confirm the structural assignments indicated in the foregoing discussion. The tricyclic olefin **10** reacts with a number of electrophiles with rearrangement by a process which can be depicted as follows.



For example, reaction of **10** with aqueous mercuric perchlorate produces after addition of chloride ion **20**, E = HgCl, N = OH, reduction of which with sodium borohydride[51] affords the tertiary alcohol **21**.[52]

(42) See C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(43) Dr. P. von R. Schleyer (personal communication) has informed us of results in his laboratory that methyl substitution at C_4 of *exo*- and *endo*-2-norbornyl sulfonates changes acetolysis rates only by a factor of *ca.* 1.2 or less.

(44) See M. C. Whiting, *Chem. Brit.*, **2**, 482 (1966).

(45) See C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).

(46) For reference it is interesting that the bridged and nonbridged B–H distances in diborane are 1.33 and 1.19 A, respectively. See W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(47) H. C. Brown and M. Gerstein, *J. Am. Chem. Soc.*, **72**, 2926 (1950).

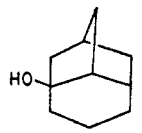
(48) (a) D. C. Kleinfelter and P. von R. Schleyer, 3rd Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1960, Abstracts, p 33; 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, Abstracts, p 43P; *Dissertation Abstr.*, 22, 428 (1961). (b) Private communication from P. von R. Schleyer.

(49) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp 184–207; H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(50) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(51) T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963).

(52) The mercuration of norbornene under similar conditions proceeds substantially without rearrangement to afford the 3-*exo*-chloromercuri-2-*exo*-norborneol (ref 51 and earlier work there cited).



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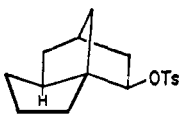
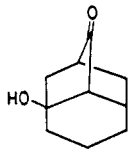


22

The nmr spectrum of **21** and the corresponding acetate indicate clearly that the hydroxyl function is tertiary. Hydrolysis of the *p*-toluenesulfonate **22** (from **12**, R = H) in aqueous acetone containing calcium carbonate also leads to **21** cleanly. Interestingly, treatment of **21** with sulfuric acid produces 1-adamantanol.

Reaction of the tricyclic olefin **10** with bromine[53] gives a dibromide which is converted by heating with an aqueous suspension of silver oxide to the bromohydrin **20**, N = OH, E = Br, which by further reaction with di-*n*-butyltin dihydride[54] yields the tertiary alcohol **21**.

The *syn* relationship of N and E in the products of type **20** is assumed by analogy with the cases of stereospecific *exo* addition of various electrophilic reagents to norbornene. The diol **20**, N = E = OH, is readily obtained by treatment of the epoxide **17** with acidic catalysts such as silica gel; chromic acid oxidation of this diol leads as expected to a keto tertiary alcohol (**23**) which shows characteristic bridge carbonyl absorption at 5.64 μ.



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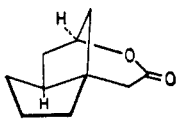

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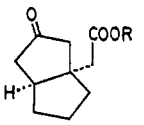

25

Along other lines, the tricyclic ketone **15** was converted by peracetic acid to the lactone **24** and thence by hydrolysis with base, oxidation with chromic acid, and subsequent reactions to a series of derivatives of the keto acid **25**, R = H. The infrared and nmr spectra[22] of **24** and the derivatives of **25** provide convincing evidence for the structures of these substances and, in consequence, for the precursors **15** and **10**. For example, the lactone **24** shows low-field resonance due to a single proton (>CHO) in the nmr spectrum at 4.72 ppm (apparent quintet) and carbonyl absorption at 5.71 μ (CCl_4), and the ketonic carbonyl of the derivatives of **25** gives rise to absorption at 5.74 μ (CCl_4) as expected for a cyclopentanone.

A series of transformations starting from the tetracyclic alcohol **18** is also of interest. Evidence for the constitution **18** for the tetracyclic alcohol comes (a) from the characteristic cyclopropyl CH absorption in the infrared at 3.28 μ[55] and in the near infrared at 1.676 μ,[56] (b) the absence of olefinic CH peaks in the nmr spectrum, and (c) oxidation by chromic acid to the corresponding ketone (**26**) which showed absorption in the infrared at 3.31 μ (cyclopropyl CH)[55] and 5.67 and 5.72 μ (*cf.* nortricyclanone carbonyl absorption at 5.66 and 5.70 μ).[57] Reaction of the ketone **26** with hydrogen bromide in methylene chloride produced a bromo ketone which from the mode of formation[58] and spectroscopic data is formulated as 5-bromo-4,5-trimethylene-2-norbornanone (**27**). This bromo ketone affords by reduction either with zinc–acetic acid, di-*n*-butyltin dihydride in tetrahydrofuran, or hydrogen and palladium on charcoal in ethanol the tricyclic ketone **15** cleanly; none of the isomeric *endo*-4,5-trimethylene-2-norbornanone could be detected.

Experimental Section

Melting points, determined using a Büchi melting point apparatus, are uncorrected. Infrared data were obtained with a Perkin-Elmer Infracord spectrophotometer, a Perkin-Elmer Model 137 sodium chloride spectrophotometer, a Perkin-Elmer Model 237 grating infrared spectrometer, and for high resolution a Cary-White Model 90 infrared spectrometer using polystyrene as a calibration standard. Near-infrared data were obtained using a Cary Model 14 spectrophotometer. Ultraviolet spectra were taken using a Cary Model 11 M ultraviolet spectrometer and a Cary Model 14 spectrophotometer. The nmr data were obtained at 60 Mc using a Varian Associates Model A-60 nmr spectrometer and are expressed as shift downfield from internal tetramethylsilane in parts per million. Vapor phase chromatography was performed using an F & M Model 300 unit with a thermal conductivity detector and an F & M Model 609 flame ionization unit. The mass spectra were recorded using a Consolidated Engineering Corp. Model 21-103 C mass spectrometer and an Associated Electrical Industries Ltd. Model MS-9 mass spectrometer. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim (Ruhr), Germany, and Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Δ^4-Pentenylcyclopentadienes 9. A 1-l., three-necked flask was equipped with a mechanical stirrer having a glass blade, a two-way stopcock to let in ammonia, a three-way stopcock for maintaining a nitrogen atmosphere, and a Y tube fitted with a pressure-equalized dropping funnel and a dewar condenser. Sodium metal (11.5 g, 0.501 g-atom) was placed in the flask under nitrogen and dissolved in distilled ammonia (500 ml).[18] The blue solution was cooled in a Dry Ice–acetone bath and stirred vigorously as dry, distilled cyclopentadiene (62 ml, 0.750 mole) was added dropwise from the pressure-equilibrated dropping funnel. As soon as the mixture became colorless, 5-bromo-1-pentene (74.5 g, 0.500 mole) was added over a 45-min period. The reaction mixture was cooled in a Dry Ice–acetone bath and stirred for 2.5 hr. After allowing the ammonia to evaporate, salt–water was added, and the aqueous mixture was extracted with ether. The ethereal layer was dried with anhydrous magnesium sulfate and filtered. The solvent was removed at room temperature with a water aspirator, and the yellow residue was distilled giving 57.9 g (86%) of the Δ^4-pentenylcyclopentadienes (**9**): bp 50–53° (7 mm). The infrared spectrum[22] of the product showed C=C stretching absorption at 6.08 and 6.23 μ; the nmr spectrum[22] showed olefinic proton peaks from 4.8 to 6.4 ppm (integrated ratio to upfield protons 5.7:8) and indicated that the mixture consisted largely of C_1 and C_2 substituted cyclopentadienes. Because of the reactivity of **9** no elemental analysis was performed. The product showed ultraviolet absorption at λ_{max} 248 mμ (ϵ 3200).

4,5-*exo*-Trimethylene-2-norbornene (10). A 300-ml, three-necked flask was equipped with a condenser, a three-way stopcock, a glass encased magnetized bar, and a pressure-equalized dropping funnel. Purified tri-*n*-butylamine (100 ml) was added to the flask under nitrogen, and the flask was placed in a silicone oil bath main-

(53) L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960).

(54) (a) H. G. Kuivila in "Advances in Organometallic Chemistry," Vol. I, F. G. A. Stone and R. West, Ed., Academic Press Inc., New York, N. Y., 1964; (b) L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

(55) (a) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966), and references therein; (b) F. J. Piehl and W. G. Brown, *J. Am. Chem. Soc.*, **75**, 5023 (1953); (c) A. R. H. Cole, *J. Chem. Soc.*, 3807, 3810 (1954); (d) M. Hanack, H. Eggensperger, and S. Kang, *Chem. Ber.*, **96**, 2532 (1963); (e) M. Horák, J. Šmejkal, and J. Farkaš, *Collection Czech. Chem. Commun.*, **28**, 2280 (1963).

(56) (a) W. H. Washburn and M. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958); (b) J. Meinwald, A. Lewis, and P. G. Gassman, *ibid.*, **84**, 977 (1962); (c) P. G. Gassman, *Chem. Ind.* (London), 740 (1962); (d) H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959); (e) H. Weitkamp and F. Korte, *Tetrahedron*, **20**, 2125 (1964); (f) H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, **30**, 2259 (1965); (g) P. G. Gassman and W. M. Hooker, *J. Am. Chem. Soc.*, **87**, 1079 (1965); (h) P. G. Gassman and F. V. Zalar, *J. Org. Chem.*, **31**, 166 (1966).

(57) R. Zbinden and H. K. Hall, *J. Am. Chem. Soc.*, **82**, 1215 (1960).

(58) H. Krieger, *Suomen Kemistilehti*, **34B**, 24 (1961); *Chem. Abstr.*, **55**, 23370*f* (1961).

tained at 200°. A solution of Δ^4-pentenylcyclopentadienes **9** (15.0 g, 0.112 mole) in tri-*n*-butylamine (100 ml) was added dropwise to the hot solvent with stirring over a period of 1 hr. The cooled solution was poured into ice-cold aqueous hydrochloric acid and extracted with two 150-ml portions of distilled trichlorofluoromethane (Freon 11). The combined organic layers were washed with cold, dilute hydrochloric acid and then sodium carbonate and dried with anhydrous magnesium sulfate. The solvent was removed by distillation at atmospheric pressure through a column consisting of a reflux condenser through which water was passed at such a rate so as to maintain good reflux. The residual yellow oil was distilled from lithium aluminum hydride, giving 9.7–14.3 g (67–96%) of tricyclic olefin **10**, bp 64–65° (26 mm). The molecular weight determined mass spectrometrically was 134. The nmr spectrum of **10**[22] exhibited peaks at 1–2 ppm (11 H), a broad singlet at 2.83 ppm due to the single bridgehead proton, and a six-peak multiplet (AB part of an ABX pattern, 2 H) due to the two olefinic protons. The infrared spectrum[22] showed olefinic CH stretch at 3.25 μ, C=C stretch at 6.23 and 6.42 μ, and a *cis*-CH=CH out-of-plane deformation band at 14.18 μ.

A small amount (3–5%) of an isomeric impurity which requires further study could be detected in the crude product by vpc analysis. An analytical sample of **10** was prepared by vpc.

Anal. Calcd for $C_{10}H_{14}$: C, 89.48; H, 10.57. Found: C, 89.75; H, 10.57.

Reaction of Tricyclic Olefin 10 with Diborane. A solution of tricyclic olefin **10** (1.34 g, 10.0 mmoles) in dry, distilled tetrahydrofuran (10 ml) was placed in a 25-ml, three-necked flask equipped with a glass stopper, a mercury sealed valve, and a glass tube with a frit on the end. The glass tube was connected to a diborane generator which consisted of a 25-ml, three-necked flask equipped with a magnetic stirring bar, a rubber serum cap, and a three-way stopcock. Distilled boron trifluoride ethereate (780 mg, 5.5 mmoles) and dry, distilled diglyme (0.7 ml) were placed in the generator flask. The air in the entire assembly was displaced by nitrogen and the diborane, produced by dropwise addition of a 1 *M* solution of sodium borohydride in diglyme (2.75 ml, 2.75 mmoles) by means of a syringe to the boron trifluoride etherate solution, was swept by a slow stream of nitrogen into the tetrahydrofuran solution of olefin **10** (cooled in an ice bath). After completion of the addition of the sodium borohydride solution, the diborane-producing solution was heated at 70–80° for 1 hr, and then the reaction flask was disconnected from the generator. The reaction solution was allowed to stand 6 hr at 0° and 36 hr at room temperature. To the cooled solution, 2.86 *M* sodium hydroxide (1.10 ml, 3.15 mmoles) was added followed by 30% hydrogen peroxide (1.1 ml, 11 mmoles). The reaction mixture was allowed to stand for 1 hr at 0° and for 2 hr at room temperature, poured into water, and extracted with ether. The ethereal extracts were stirred for 1 hr with 5% palladium on charcoal, dried ($MgSO_4$), concentrated, and distilled, giving 990 mg (60%) of a mixture of alcohols. The mixture was analyzed by vpc using a 12-ft 5% Carbowax 20M column and found to consist of **11**, R = H (70%), **12**, R = H (17%), and **14** (13%).

In another run only **11**, R = H (74%), and **12**, R = H, were obtained, but an aliquot of this reaction mixture to which boron trifluoride etherate was added gave **14** in addition to these alcohols.

Reaction of Tricyclic Olefin 10 with Disiamylborane. In a dry, 250-ml flask equipped with a serum cap were placed 2-methylbutene-2 (23.1 g, 0.329 mole), dry, distilled diglyme (50 ml), and sodium borohydride (4.70 g, 0.124 mole) under nitrogen. The mixture was stirred vigorously and cooled in an ice bath as distilled boron trifluoride etherate (23.5 g, 0.166 mole) was added dropwise by means of a syringe over a period of 45 min. The mixture was allowed to stand at 0° for 15–18 hr. Tricyclic olefin **10** (5.52 g, 0.0412 mole) dissolved in diglyme (5 ml) was added to the semisolid material. The mixture was stirred for 30 hr at 0° and for 24 hr at room temperature. The reaction mixture was oxidized by cautiously adding 3 *N* sodium hydroxide (50 ml) followed by dropwise addition of 30% hydrogen peroxide (50 ml). After stirring for 5 hr, the mixture was diluted with water and extracted twice with ether. The combined extracts were washed four times with cold water, once with sodium bisulfite solution, and once again with water, dried with anhydrous magnesium sulfate, concentrated, and distilled, giving 3.84 g (62%) of a mixture of alcohols, bp 62–63° (0.02 mm). The mixture was analyzed by vpc and found to consist of **12**, R = H (8%), and **11**, R = H (92%). Part of this mixture of alcohols (0.912 g, 6.0 mmoles) and 3,5-dinitrobenzoyl chloride (1.53 g, 6.6 mmoles) were heated in dry, distilled pyridine (6 ml) until solution was effected. The solution was stirred for 3.5 hr at room temperature, and the mixture was dissolved in benzene, washed with cold, dilute hydrochloric acid (9.0 ml of concentrated HCl in 300 ml of water), water, and saturated sodium bicarbonate solution, dried (K_2CO_3), and concentrated, leaving 1.91 g (92% of a mixture of esters. The mixture was recrystallized twice from *n*-hexane, yielding 1.31 g (70%) of the 3,5-dinitrobenzoate **11**, R = $(NO_2)_2C_6H_3CO$, mp 121.5–122.5°; λ ($CHCl_3$) 3.22, 3.39, 3.49, 5.81 (C=O), 6.15 (C=C), 6.50, 7.49, 7.82, 8.59 μ.

Anal. Calcd for $C_{17}H_{18}N_2O_6$: C, 58.96; H, 5.24; N, 8.09. Found: C, 58.96; H, 5.35; N, 8.10.

The purified 3,5-dinitrobenzoate of **11**, R = H (1.23 g, 3.54 mmoles), methanol (5.9 ml), and 5 *N* sodium hydroxide (2.9 ml) were refluxed under nitrogen for 1 hr. The mixture was added to water and repeatedly extracted with ether. The ethereal extracts were dried with anhydrous potassium carbonate and concentrated, leaving **11**, R = H, in quantitative yield, mp 45–49°.

The infrared spectrum of **11**, R = H (neat), showed hydroxyl absorption at 2.96 μ (broad); the nmr spectrum ($CDCl_3$) exhibited a doublet of doublets at 3.88 ppm due to >CHO (1 H), a sharp peak due to OH at 2.88 ppm, a broad singlet due to bridgehead CH (1 H) at 2.12 ppm, and many peaks due to the remaining protons at 2.0–1.0 ppm.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.62; H, 10.56.

The alcohol **12**, R = H, was isolated as follows. The mother liquor from the first recrystallization of the mixture of 3,5-dinitrobenzoates of alcohols **11** and **12** was concentrated. Hydrolysis of the mixture of esters and preparative vpc of the mixture of alcohols gave **12**, R = H: hydroxyl absorption at 2.65 and 2.8 μ; nmr ($CDCl_3$): 1.0–2.3 (multiplet, 14 H), 2.65 (singlet, 1 H), and 3.60 ppm (broadened doublet, J = 6.5 cps, 1 H).[22]

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.60; H, 10.56.

***exo*-4,5-Trimethylene-2-*exo*-norbornyl *p*-Toluenesulfonate (11, R = Ts).** To a solution of the tricyclic *exo* alcohol **11**, R = H (76.9 mg, 0.506 mmole), in dry, distilled pyridine (1.25 ml), *p*-toluenesulfonyl chloride (250.6 mg, 1.32 mmoles) was added. The solution was allowed to stand for 24 hr at room temperature. Four drops of water were added, and the solution was allowed to stand for 0.5 hr without cooling. The solution was poured into water and ether, and the aqueous phase extracted again with ether. The combined extracts were washed with water, sodium bisulfate solution, and water again, dried ($MgSO_4$), and concentrated, leaving 150 mg (97%) of 4,5-*exo*-trimethylene-2-*exo*-norbornyl tosylate (**11**, R = Ts), mp 66.5–68°; $\lambda_{max}^{AcOH,0.01MNaOAc}$ 262.3 mμ (ϵ 554), 267.5 mμ (ϵ 500), and 273.2 mμ (ϵ 446). The infrared and nmr spectra[22] agreed with the assigned structure.

Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.61; H, 7.24; S, 10.47. Found: C, 66.75; H, 7.09; S, 10.63.

***exo*-4,5-Trimethylene-2-norbornanone (15).** To a stirred solution of tricyclic alcohol **11**, R = H (152 mg, 1.00 mmole), in acetone (2.5 ml) cooled in an ice bath, oxidizing agent (6.68 g of chromium trioxide and 5.75 ml of concentrated sulfuric acid diluted to 100 ml of solution with water) was added dropwise. The addition was continued until the color of the reagent was not discharged within 0.5 hr at room temperature. The excess oxidant was destroyed with isopropyl alcohol. The mixture was diluted with water and repeatedly extracted with ether. The ethereal extracts were washed with saturated aqueous sodium bicarbonate solution and water, dried with anhydrous potassium carbonate, and concentrated, leaving 143 mg (95%) of tricyclic ketone **15**; the infrared spectrum showed ν (CCl_4) 1749 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.13; H, 9.50.

To the tricyclic ketone **15** (24.3 mg, 0.162 mmole) dissolved in 95% ethanol (0.4 ml), a solution of acidic 2,4-dinitrophenylhydrazine (1.0 ml) reagent was added. The reaction mixture was allowed to stand for several hours at room temperature. Filtration of the mixture gave 48.1 mg (90%) of a yellow solid. Two recrystallizations from acetonitrile gave yellow crystals of the 2,4-dinitrophenylhydrazone of tricyclic ketone **15**, mp 172–174°; λ ($CHCl_3$) 2.97, 3.35, 6.17, 6.29, and 7.50 μ.

Anal. Calcd for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.14; H, 5.48; N, 17.13.

***exo*-4,5-Trimethylene-2-*endo*-norborneol (16, R = H).** To a solution of the tricyclic ketone **15** (30.0 mg, 0.200 mmole) in methanol (1.0 ml) cooled in an ice bath was added sodium borohydride (37.1 mg, 0.981 mmole) dissolved in cold methanol (2.0 ml) with stirring over a period of 30 min. The solution was stirred at 0° for 1 hr and at room temperature for 2 hr. The mixture was poured into water and twice extracted with 2:1 *n*-pentane–methylene

chloride solution. The combined organic extracts were washed three times with water, dried ($MgSO_4$), and concentrated, giving 29.7 mg (97%) of tricyclic *endo* alcohol **16**, R = H. The solid was dissolved in *n*-pentane at room temperature and cooled to 0°. Recrystallization twice in this manner gave colorless crystals, mp 56–58°. The molecular weight determined mass spectrometrically was 152.1200 (calcd for $C_{10}H_{16}O$: 152.1201). The nmr spectrum[22] of **16**, R = H, showed a multiplet (1 H) due to >CHO at 4.23 ppm, a sharp peak due to hydroxyl at 3.2 ppm, and many peaks due to the remaining protons at 0.85–2.4 ppm; the infrared spectrum showed the expected OH stretching absorption at 2.65 and 2.95 μ in CCl_4.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.31; H, 10.65.

***p*-Toluenesulfonate 16, R = Ts.** The *endo* tricyclic alcohol **16**, R = H (39.4 mg, 0.259 mmole), dissolved in pyridine (0.65 ml) was allowed to react with *p*-toluenesulfonyl chloride (130.6 mg, 0.685 mmole) as described for the preparation of **11**, R = Ts, giving 74.4 mg (96%) of a solid. Two recrystallizations from *n*-pentane gave colorless crystals of 4,5-*exo*-trimethylene-2-*endo*-norbornyl *p*-toluenesulfonate (**16**, R = Ts), mp 50–51.5°; $\lambda_{max}^{AcOH,0.01\,MNaOAc}$ 262.4 mμ (ϵ 544), 267.6 mμ (ϵ 492), and 273.4 mμ (ϵ 438). The infrared and nmr spectra[22] were consistent with the assigned structure.

Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.61; H, 7.24; S, 10.47. Found: C, 66.89; H, 7.14; S, 10.55.

Tricyclic *exo* Acetate 11, R = CH_3CO. To a solution of *exo* alcohol **11**, R = H (50.6 mg, 0.333 mmole), in dry, distilled pyridine (0.55 ml) cooled in an ice bath was added acetic anhydride (0.27 ml). After standing at room temperature for 74 hr, the solution was poured into water and twice extracted with *n*-pentane. The pentane extracts were washed with aqueous copper sulfate solution, water, aqueous sodium bicarbonate solution, and water, dried ($MgSO_4$), and concentrated, giving 61.0 mg (94%) of 4,5-*exo*-trimethylene-2-*exo*-norbornyl acetate (**11**, R = CH_3CO). The infrared spectrum[22] showed carbonyl absorption at 5.73 μ due to acetate; the nmr spectrum showed a doublet of doublets (1 H) due to >CHO at 4.70 ppm, a sharp acetyl singlet (3 H) at 2.02 ppm, a broad singlet at 2.23 ppm (1 H) due to the bridgehead proton at C_1, and additional peaks upfield.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.42; H, 9.59.

Tricyclic *endo* Acetate 16, R = CH_3CO. The *endo* alcohol **16**, R = H (155.5 mg, 1.023 mmoles), was acetylated as described above, giving 190.9 mg (96%) of 4,5-*exo*-trimethylene 2-*endo*-acetate **16**, R = CH_3CO; the infrared (neat) spectrum showed an ester carbonyl at 5.73 μ; the nmr spectrum showed a broad peak (1 H) due to >CHO at 4.98 ppm and other peaks upfield including a sharp acetyl signal (3 H, 2.0 ppm). The molecular weight determined mass spectrometrically was 194.1301 (calcd for $C_{12}H_{18}O_2$: 194.1306).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.74; H, 9.17.

Tricyclic Epoxide 17. A 0.30 *M* solution of monoperphthalic acid[59] in ether (100 ml, 30 mmoles) was added to tricyclic olefin **10** (1.79 g, 13.3 mmoles) cooled in a salt–ice bath. After standing for 62 hr at 0°, the solution was poured into cold 10% aqueous sodium hydroxide solution. The ethereal solution was washed twice with 10% aqueous sodium hydroxide solution and water, dried ($MgSO_4$), concentrated, and distilled, giving 1.64 g (82%) of tricyclic epoxide **17**, bp 45° (0.6 mm).

The nmr spectrum[22] of **17** (CCl_4) showed one proton of the oxirane ring as a sharp doublet at 2.7 and 2.82 ppm and the other as a broadened doublet at 2.92 and 2.99 ppm and a broad singlet due to the bridgehead proton at C_1 at 2.41 ppm (1 H), as well as other peaks upfield.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.01; H, 9.47.

Reduction of Tricyclic Epoxide 17 with Lithium Aluminum Hydride. A mixture of the tricyclic epoxide **17** (31 mg, 0.20 mmole), powdered lithium aluminum hydride (24 mg, 0.64 mmole), and dry, distilled glyme (1.0 ml) was stirred at reflux for 30 hr. Water was cautiously added, and the mixture was repeatedly extracted with ether. The ethereal extracts were dried ($MgSO_4$) and concentrated, giving an oil which was analyzed by vpc. The oil was found to be a mixture of **11**, R = H (33%), **12**, R = H (63%), and **14** (4%).

Reaction of Tricyclic Epoxide 17 with Aluminum Chlorohydride Reagent. A mixture of lithium aluminum hydride (86.6 mg, 2.28 mmoles) and dry ether (2.0 ml) was refluxed for 30 min. The cooled lithium aluminum hydride slurry was added to a solution of anhydrous aluminum chloride (262 mg, 1.97 mmoles) in dry ether (2.0 ml) cooled in an ice bath. The mixture was stirred for a period of 0.5 hr at room temperature. A solution of tricyclic epoxide **17** (14.7 mg, 0.0988 mmole) in dry ether (0.5 ml) was added to the mixed hydride reagent, and the mixture was refluxed for 22 hr. The reaction mixture was hydrolyzed with water and extracted with ether. The ethereal extracts were dried ($MgSO_4$) and concentrated, giving 13.5 mg (90%) of a mixture of alcohols. The mixture wa found to consist of **11**, R = H (24%), and **14** (76%) by vpc analysis.

Isolation of Rearranged Alcohol 14. Alcohols **11**, R = H, and **14** were separated by preparative vpc using a 12-ft 5% Carbowax 20M column. The alcohol **14** was obtained as colorless crystals, mp 102–113°; the nmr spectrum ($CDCl_3$) showed peaks at 0.8–2.5 (multiplet, 14 H), 3.79 (singlet, 1 H), and 3.94 ppm (singlet, 1 H); in CS_2 it showed 0.8–2.5 (multiplet, 14 H), 3.83 (singlet, 1 H), and 4.40 ppm (singlet, 1 H). The molecular weight determined mass spectrometrically was 152.1198 (calcd for $C_{10}H_{16}O$: 152.1201).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.56; H, 10.73.

Oxidation of 14. Rearranged alcohol **14** (15.7 mg, 0.103 mmole) was oxidized as described for the oxidation of the *exo* alcohol **11**, R = H, to the tricyclic ketone **15**, giving 11.7 mg (76%) of tricyclic ketone, mp 119–130°; infrared (CCl_4) absorption due to carbonyl at 5.63 μ. The molecular weight determined mass spectrometrically was 150.1047 (calcd for $C_{10}H_{14}O$: 150.1045).

Mercuration of Tricyclic Olefin 10 to Give 20, E = HgCl, N = OH. To a stirred solution of tricyclic olefin **10** (134 mg, 1.00 mmole), 61.3% perchloric acid (164 mg, 1.00 mmole), water (0.8 ml), and acetone (0.8 ml), freshly prepared yellow mercuric oxide (217 mg, 1.00 mmole) was added portionwise. After stirring the mixture for 5 hr, the mercuric oxide had completely dissolved. The acetone was removed by evaporation, and the mixture was added to a solution of sodium chloride (117 mg, 2.00 mmoles) in water (1.0 ml). The mixture was shaken for a short time and then filtered with suction. The solid was washed with a small amount of water and dried under vacuum, giving 382 mg (99%) of a solid. Recrystallization from acetone gave colorless crystals of oxymercurial **20**, E = HgCl, N = OH, mp 198°; λ (KBr) 2.82, 2.92, 3.38, 3.49, 6.83, 6.94, 7.51, 8.18, 9.02, 9.31, and 11.23 μ; ν (CCl_4) 3596 cm^{-1} (OH).

Anal. Calcd for $C_{10}H_{15}ClHgO$: C, 30.99; H, 3.91; Cl, 9.16; Hg, 51.81. Found: C, 31.24; H, 3.92; Cl, 9.03; Hg, 51.73.

Reduction of Oxymercurial 20, E = HgCl, N = OH, with Sodium Borohydride. To a stirred mixture of the oxymercurial (350 mg, 0.90 mmole) and 0.1 *N* sodium hydroxide in methanol (5 ml) cooled in an ice bath was added sodium borohydride (450 mg, 1.2 mmoles) in portions over a period of 1.25 hr. The mixture was refluxed for 3 hr, slowly poured into 10% aqueous hydrochloric acid solution, and extracted five times with methylene chloride. The extracts were dried ($MgSO_4$) and concentrated, giving 133 mg (98%) of a colorless, volatile solid. Sublimation at 85 mm gave colorless crystals of tertiary alcohol **21**, mp 161–162°; infrared absorption (in CCl_4) due to OH at 2.65 (sharp) and 2.95 (broad); nmr peaks (CCl_4) between 1.2 and 2.4 ppm (multiplets) only (no peaks downfield).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.15; H, 10.63.

A solution of tertiary alcohol **21** (69 mg, 0.45 mmole), acetic anhydride (460 mg, 4.5 mmoles), and dry pyridine (360 mg, 4.6 mmoles) under nitrogen was maintained at 78–80° for 65 hr. The dark brown solution was poured into water and extracted with *n*-pentane. The pentane extract was washed twice with 2 *N* copper sulfate solution and water, dried ($MgSO_4$), and concentrated, giving 76 mg (76%) of the acetate of **21**; infrared absorption due to carbonyl at 5.73 μ; nmr (CCl_4) 1.0–2.4 ppm (multiplet; singlet at 1.79 ppm) and no peaks downfield.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.34; H, 9.42.

Tricyclic Tosylate 22. To a solution of alcohol **12**, R = H (12.5 mg, 0.0822 mmole), in dry, distilled tetrahydrofuran (0.25 ml) under nitrogen and cooled in an ice bath was added a 1.6 *M* *n*-butyllithium solution (0.06 ml, 0.096 mmole) in hexane. The solution was stirred at 0° for a period of 30 min. A solution of *p*-toluenesulfonyl chloride (19.3 mg, 0.10 mmole) in dry, distilled tetrahydrofuran (0.25 ml) was added. The solution was stirred for 5.7 hr at 0° and then poured into water. The mixture was extracted with ether, and the extracts were washed with water, 10%

(59) G. B. Payne, *Org. Syn.*, **42**, 77 (1962).

aqueous sodium bicarbonate solution and brine, dried ($MgSO_4$), and concentrated, giving 25.3 mg (100%) of tosylate **22**; λ (neat) 3.42, 6.24, 7.22, 8.46, and 12.27 μ.

Hydrolysis of Tricyclic Tosylate 22. A mixture of tricyclic tosylate **22** (25.3 mg, 0.0827 mmole), 75% aqueous acetone (1 ml), and excess calcium carbonate was stirred at room temperature for a period of 20 hr. The reaction mixture was poured into water and repeatedly extracted with ether. The ethereal extracts were washed with water, dried, and concentrated, giving 11.9 mg (95%) of essentially pure rearranged tertiary alcohol **21**. The product, as purified by preparative vpc, exhibited identical infrared absorpton as the product obtained as described above from **20**, E = HgCl, N = OH. The alcohols prepared by the two methods had the same melting point and the melting point of mixtures was undepressed. Both alcohols showed identical behavior on tlc on silica gel and vpc on a 12-ft 5% Carbowax 20M column.

Bromination of Tricyclic Olefin 10. To a solution of tricyclic olefin **10** (134 mg, 1.00 mmole) in methylene chloride (0.5 ml) cooled in a salt–ice bath was added a solution of bromine (160 mg, 1.00 mmole) in methylene chloride (0.5 ml) dropwise with stirring. The color of the reagent was immediately discharged with each drop added to the olefin solution. After completion of the addition of the bromine, the solution was concentrated, giving 280 mg (97%) of a mixture consisting of a monobromide and mainly dibromide; λ (neat) 3.38, 6.81, 6.95, 7.70, 7.96, 9.03, 12.61, and 13.61 μ; nmr (CCl_4) 1.0–2.6 (multiplet, 19 H) and 4.07 ppm (singlet, 3 H). The mixture gave an immediate precipitate on exposure to alcoholic silver nitrate.

Formation of Bromohydrin 20, E = Br, N = OH. A mixture of freshly prepared silver oxide (200 mg, 0.87 mmole), crude dibromide (110 mg, 0.38 mmole), and water (2 ml) was refluxed for 17 hr. The mixture was filtered, diluted with water, and extracted with ether. The ethereal extract was dried ($MgSO_4$) and concentrated, giving 50 mg (57%) of a mixture which consisted mainly of bromo alcohol **20**, N = OH, E = Br: λ (neat) 2.79, 2.90, 3.40, 5.89, 6.82, 6.94, 7.32, and 9.01 μ.

This mixture gave a positive Beilstein test but did not give a precipitate on boiling for several minutes with a solution of silver nitrate in alcohol.

Reduction of Bromo Alcohol 20, N = OH, E = Br. To a solution of crude bromo alcohol (36 mg, 0.16 mmole) in dry, distilled tetrahydrofuran (1.0 ml) under nitrogen was added di-*n*-butyltin dihydride (0.2 ml, 1.0 mmole) by means of a syringe. The solution was irradiated with light from a sun lamp for 5 min and allowed to stand at room temperature for 19 hr. 2-Bromopropane (0.1 ml) was added, and the solution was stirred for 1 hr. A 20% aqueous solution of sodium potassium tartrate (4 ml) and *n*-pentane was added, the mixture was stirred for 3 hr and filtered through Celite, and the pentane layer was separated. The pentane solution was washed with aqueous sodium potassium tartrate solution and water, dried ($MgSO_4$), and concentrated, giving 24 mg (99%) of a mixture of two compounds. The major product was isolated by preparative vpc (12 mg was collected) and shown to have identical behavior on tlc and vpc with tertiary alcohol **21** prepared by reduction of oxymercurial **20**, E = HgCl, N = OH. The two alcohols had identical infrared spectra and the same melting point; mixtures of the two alcohols had undepressed melting point.

Rearrangement of Tricyclic Epoxide 17 on Silica Gel. The crude tricyclic epoxide **17** (230 mg) was chromatographed over silica gel (Davison, 20 g) using a long column (10 × 300 mm). Nothing was eluted by *n*-pentane (200 ml), 20% methylene chloride–*n*-pentane (100 ml), or 50% methylene chloride–*n*-pentane (100 ml). Methylene chloride (300 ml) eluted an oil (30 mg), and ethyl ether eluted first (50 ml) an oil (22 mg) and then (100 ml) a colorless solid (73 mg). The colorless solid eluted by ethyl ether was the diol **20**, E = N = OH, mp 159–161°; λ (CH_2Cl_2) 2.93 (OH), 3.36, 6.83, 7.03, 8.32, 8.95, 9.26, 9.53, and 11.03 μ; nmr (CCl_4) 1.2–2.2 (multiplet, 13 H), 3.88 (singlet, 1 H), and 4.64 ppm (singlet, 2 H); nmr ($CDCl_3$) 1.2–2.2 (multiplet, 13 H), 3.86 (singlet, 2 H), and 3.98 ppm (singlet, 1 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.92; H, 9.63.

The diol **20**, E = N = OH, did not react with periodic acid.

Acid-Catalyzed Hydrolysis of Tricyclic Epoxide 17. A stirring mixture of tricyclic epoxide **17** (150.3 mg, 1.00 mmole), water (0.6 ml), and 72% perchloric acid (1 drop) was maintained at 60° for a period of 1 hr. The mixture was neutralized with 0.1 *N* sodium hydroxide, diluted with water, and extracted three times with ether. The ethereal extracts were dried ($MgSO_4$) and concentrated; the solid residue was sublimed twice and recrystallized twice from *n*-hexane, giving 22 mg (13%) of diol **20**, E = N = OH, mp 148–150°, having the same infrared spectrum as the product from the previous procedure.

Hydroxy Ketone 23. Diol **20** (18.6 mg, 0.111 mmole) was oxidized as described for the oxidation of **11**, R = H, to tricyclic ketone **15**, giving 9.1 mg (50%) of hydroxy ketone **23**, infrared absorption (CCl_4) 5.64 μ. The molecular weight determined mass spectrometrically was 166.0992 (calcd for $C_{10}H_{14}O_2$: 166.0994).

Lactone 24. Anhydrous sodium acetate (102 mg) was added to peracetic acid ("Becco 40%," 10 g), and this solution (5 ml) was diluted with methylene chloride (10 ml). The methylene chloride solution was filtered through cotton and titrated (4.50 *N*). To the tricyclic ketone **15** (115 mg, 0.769 mmole) was added buffered peracetic acid in methylene chloride (2.0 ml, 9.0 mequiv). After allowing the reaction mixture to stand for 85 hr at 26–28°, additional peracetic acid solution (1.0 ml, 4.5 mequiv) was added, and the reaction mixture was allowed to stand for another 96 hr at 26–28°. The mixture was poured into water and extracted three times with ether. The ethereal extracts were washed with sodium bicarbonate solution, sodium bisulfite solution, and water, dried ($MgSO_4$), concentrated, and distilled, giving 102 mg (80%) of lactone **24**; infrared absorption (CCl_4) due to carbonyl at 5.71 μ, no OH absorption; nmr spectrum (CS_2): peak at 4.72 ppm (apparent quintet, 1 H) due to >CHOCO and other peaks upfield between 1.0 and 2.9 ppm.[22]

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.55; H, 8.54.

Hydrolysis and Oxidation of 24. A solution of lactone **24** (645 mg, 3.88 mmoles) and potassium hydroxide (5.67 g, 0.101 mole) in methanol (180 ml) was refluxed for 13 hr. Evaporation of most of the methanol, dilution with water, ether extraction (discarded), dropwise addition of 2 *N* sulfuric acid (99 ml, 0.198 mole) at 0°, and extraction with ether gave 688 mg (96%) of hydroxy acid, mp 90–98°, which was methylated with ethereal diazomethane (3 hr), giving 685 mg (91%) of hydroxy ester which then was oxidized by chromic acid to give 562 mg (83%) of keto ester **25**, R = CH_3. This ester showed carbonyl absorption due to ketone and ester functions at 5.74 μ (in CCl_4), indicating that the ketone function was present in a five-membered ring. A considerable number of further transformations of this substance are given in the thesis cited in ref 22.

Transformation of the Epoxide 17 to the Tetracyclic Alcohol 18. To a stirred solution of dry, distilled diethylamine (445 mg, 6.01 mmoles) in sodium-dried benzene (2.8 ml) under nitrogen and cooled in an ice bath was added a 1.6 *M* solution of *n*-butyllithium in hexane (2.8 ml, 4.48 mmoles) by means of a syringe. The mixture was stirred for 20 min. A solution of tricyclic epoxide **17** (399 mg, 2.66 mmoles) in sodium-dried benzene (2.8 ml) was added to the lithium diethylamide mixture. The reaction mixture was stirred and refluxed for a period of 48 hr. The mixture was cooled, poured into ice–water, and extracted twice with ether. The combined ethereal extracts were washed with saturated aqueous ammonium chloride solution and water, dried ($MgSO_4$), concentrated, and distilled [50–60° (0.4 mm)], giving 342 mg (86%) of tetracyclic alcohol **18**, mp 56–70°; near-infrared (CCl_4) absorption at 1.676 μ (ε 0.38); nmr (CCl_4) 1.0–2.1 (multiplet, 14 H), 3.86 (singlet, 1 H), and 4.45 ppm (singlet, 1 H). The molecular weight determined mass spectrometrically was 150.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.96; H, 9.32.

The tetracyclic alcohol **18** (50.3 mg, 0.335 mmole) was acetylated using acetic anhydride–pyridine giving 63.4 mg (98%) of the corresponding acetate, infrared absorption at 5.73 μ; nmr ($CDCl_3$) 1.1–2.2 (multiplet, 15 H) and 4.72 ppm (multiplet, 1 H). The molecular weight determined mass spectrometrically was 192.1138 (calcd for $C_{12}H_{16}O_2$: 192.1150).

Anal. Calcd for $C_{12}H_{15}O_2$: C, 74.97; H, 8.39. Found: C, 74.81; H, 8.42.

From the tetracyclic alcohol **18** (30.4 mg, 0.203 mmole) a tosylate was prepared using *p*-toluenesulfonyl chloride (38.1 mg, 0.200 mmole in sodium-dried ether (0.5 ml) and powdered potassium hydroxide (30.2 mg, 0.539 mmole) added portionwise at −10°. The mixture was stirred at 0–5° for a period of 12 hr, poured into water, and extracted with ether. The ethereal extract was dried ($MgSO_4$) and concentrated, giving 54.0 mg (88%) of a colorless solid. Two recrystallizations from *n*-pentane gave colorless crystals of tosylate **18**, mp 66.5–69°; $\lambda_{max}^{AcOH,0.01\,MNaOAc}$ 262.0 mμ (ε 486), 267.4 mμ (ε 423), and 273.0 mμ (ε 350). The molecular weight determined mass spectrometrically was 304.1137 (calcd for $C_{17}H_{20}O_3S$: 304.1133).

Reaction of *p*-Toluenesulfonate of 18 with Sodium Borohydride in Aqueous Diglyme. A solution of the *p*-toluenesulfonate of **18** (88.8 mg, 0.292 mmole), sodium borohydride (94.7 mg, 2.51 mmoles), and sodium hydroxide (24.5 mg, 0.613 mmole) in 65 vol. % aqueous diglyme (0.6 ml) was stirred for 16 hr at room temperature. The solution was poured into water and extracted twice with trichlorofluoromethane (Freon 11). The extracts were washed with water, dried ($MgSO_4$), and concentrated, giving a mixture of products. The mixture was analyzed by vpc and found to consist of tetracyclic alcohol **18** (75%) and a 9:1 mixture of hydrocarbons (25%). The minor hydrocarbon had the same retention time on a 200-ft tricyanoethoxypropane capillary (0.011 in.) column as tricyclic olefin **10**, and the major hydrocarbon was 1,2-trimethylenenortricyclene, which was obtained pure by preparative vpc; nmr (CS_2) 0.9–2.2 ppm (multiplet). The molecular weight determined mass spectrometrically was 134.1094 (calcd for $C_{10}H_{14}$: 134.1095).

4,5-Trimethylenenortricyclanone (26). The alcohol **18** (197 mg) was oxidized as described for the oxidation of **11**, R = H, to **15**, giving 132 mg (70%) of tetracyclic ketone **26**, $\lambda_{max}^{95\%\ EtOH}$ 271 mμ (ε 46); infrared (CCl_4)[22] carbonyl absorption 5.67 and 5.72 μ; nmr (CCl_4) 1.2–2.2 ppm (multiplet). The molecular weight determined mass spectrometrically was 148.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.34; H, 8.23.

Tetracyclic ketone **26** was not reduced by zinc in acetic acid at reflux nor by hydrogen and 10% palladium on charcoal in acetic acid at room temperature at 1 atm.

5-Bromo-4,5-trimethylenenorbornanone (27) and Its Reduction. A 0.36 *M* solution of anhydrous hydrobromic acid (38 ml, 13.7 mmoles) in methylene chloride was added to tetracyclic ketone **26** (1.19 g, 8.04 mmoles). After standing at room temperature for a period of 17 hr, the solution was concentrated, giving 1.65 g (90%) of a brown semisolid. Sublimation gave colorless crystals of bromo ketone **27**, mp 146–148°; infrared absorption (CCl_4) 5.70 μ; nmr (CCl_4) 1.5–2.7 ppm (multiplet). The mass spectrum showed two peaks of equal intensity at 228 and 230.

Reduction of **27** with the following reagents gave tricyclic ketone **15**: zinc in acetic acid, di-*n*-butyltin dihydride in tetrahydrofuran, and hydrogen and 10% palladium on charcoal in 95% ethanol. The products were analyzed by infrared absorption and vpc with a 12-ft 5% Carbowax 20M column.

Acetolysis Products from 4,5-*exo*-Trimethylene-2-*exo*-norbornyl *p*-Toluenesulfonate (11, R = Ts). A solution of the *exo*-*p*-toluenesulfonate **11**, R = Ts (102.3 mg, 0.334 mmole), in 0.010 *M* sodium acetate in anhydrous acetic acid solution (60 ml) was stirred and maintained at 81–83° for 5 hr (*ca.* ten half-lives). The cooled solution was diluted with water, neutralized with sodium carbonate, and repeatedly extracted with ether. The combined ether extracts were washed with water, saturated aqueous sodium bicarbonate solution, and water, dried ($MgSO_4$), concentrated, analyzed by vpc, and distilled, giving 55.4 mg (85%) of tricyclic *exo* acetate **11**, R = CH_3CO. This product had the same vpc retention time, the same infrared spectrum, and the same nmr spectrum as the *exo* acetate **11**, R = CH_3CO, prepared by acetylation of **11**, R = H. A considerable study was made of various columns for vpc analysis of mixtures of **11**, R = H, and **16**, R = H, and also of mixture of the corresponding acetates; this analysis was not possible using long 0.25- or 0.125-in. columns with a large variety of stationary phases (both polar and nonpolar), since the chromatographic behavior of the *exo*, *endo* isomers was essentially identical. Slight separation was noted using tricyanoethoxypropane as stationary phase with the acetates **11**, R = CH_3CO, and **16**, R = CH_3CO, and it proved possible to achieve acceptable resolution using this stationary phase in a 200-ft, 0.11 in. capillary column at 100°. The total mixture obtained from the above experiment before distillation was analyzed in this way. Peaks were observed at the following retention times (min): 5.3 (3.5%), 5.5 (sh, *ca.* 1%), 37–39.5 (4%, broad, includes two or more unresolved), 41.3 (91.5%, corresponds to **11**, R = CH_3CO, the major product). It seems likely, though by no means certain, that the broad peak at 37–39 min contains the *endo* acetate **16**, R = CH_3CO, as a component, since the latter exhibits a peak at 39 min under the conditions of this analysis. The tricyclic olefin **10** under these conditions exhibits a retention time of 5.3 min.

Acetolysis of 4,5-*exo*-Trimethylene-2-*endo*-norbornyl *p*-Toluenesulfonate (16, R = Ts). A solution of the *p*-toluenesulfonate **16**, R = Ts (99.0 mg, 0.324 mmole), in 0.010 *M* sodium acetate in anhydrous acetic acid solution (60 ml) was stirred and maintained at 100–103° for 5 hr (*ca.* ten half-lives). After neutralizaton and ether work-up, the product was analyzed by vpc and distilled, giving 55.2 mg (88%) of tricyclic *exo* acetate **11**, R = CH_3CO. This product had the same retenton time on vpc, the same infrared spectrum, and the same nmr spectrum as prepared by acetylation of **11**, R = H. The vpc analysis of the total product before distillation was performed on the 200-ft capillary tricyanoethoxypropane column at 100° under the same conditions as used for the previously described analysis. The vpc product analysis, which was very similar to that for the acetolysis of **11**, R = Ts, revealed components at the following retention times (min): 5.3 (2.5%), 5.5 (1.5%), 37–39.5 (4%, broad), and 42.2 (92%), the last of which corresponds to **11**, R = CH_3CO.

Kinetic Data. The method of Swain and Morgan[36] was used with a Cary Model 14 spectrophotometer equipped with a thermostated cell compartment. Acetolyses were conducted in quartz cells sealed with tightly fitting Teflon stoppers. The *p*-toluenesulfonate was dissolved in *ca.* 10 ml of anhydrous acetic acid (dried with molecular sieves and distilled) containing fused sodium acetate at a concentration of 0.01 *M*. Excellent first-order rate constants were obtained (for tables of original data see thesis cited in ref 22). Measurements of the rate constants for acetolysis of *exo*- and *endo*-norbornyl *p*-toluenesulfonates gave results in excellent agreement with values previously obtained by titrimetric analysis.[37]

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