(d, J = 4.5 Hz, CCH$_3$), 2.3 (d, J = 14.25 Hz, PCH$_3$), 1.5–2.1 (m, ring protons), 7.5–8.1 (m, PC$_6$H$_5$).

Anal. Calcd for $C_{12}H_{18}PBr$: C, 52.76; H, 6.64. Found: C, 52.51; H, 6.85.

Reactions of **7a** and **7b** with sodium hydroxide were carried out as for **5a**. Vpc analysis of the organic layer obtained by azeotropic distillation of the reaction mixture showed only benzene to be present. Distillation of the oxide mixture derived from 2.0 g of **7a** or **7b** gave 0.40 and 0.45 g, respectively, both of bp 70–80° (0.1 mm) and mp 45–57°. The nmr spectra were identical in every respect: nmr (CCl$_4$, TMS) δ 1.07 (d, J = 6 Hz, CCH$_3$), 1.13 (d, J = 5.3 Hz, CCH$_3$), 1.5 (d, J = 12.5 Hz, PCH$_3$), 1.3–2.6 (m, ring protons). The two oxide mixtures were separately reduced with phenylsilane and quaternized with benzyl bromide, each giving a phosphonium salt mixture of mp 154–164°. Comparison of the nmr spectra of these mixtures with those of known mixtures prepared from pure cis and trans isomers of 1-benzyl-1,3-dimethylphospholanium bromide[2] showed the unknown mixtures to consist of about equal quantities of the two isomers.

Synthesis of 3-Methyl-1,1-diphenylphospholanium Hexafluorophosphate (8).—A mixture of 50.0 g (0.217 mol) of 1,4-dibromo-2-methylbutane and 40.2 g (0.108 mol) of tetraphenyldiphosphine in 270 ml of *o*-dichlorobenzene was added dropwise to 750 ml of refluxing *o*-dichlorobenzene over a period of 3 hr. The solvent (800 ml) was removed by distillation, the residue was extracted with water, and the water extract was evaporated, leaving 41.7 g of a dark, acidic oil, from which crystals could not be obtained. A 27-g portion of this oil was dissolved in water and titrated to neutrality with 70 ml of 1 N sodium bicarbonate, extracted with ether and then with chloroform. Evaporation of the chloroform extract yielded 16 g of a dark glassy oil of which a 7-g portion was dissolved in water and to which a saturated solution of 4.0 g of potassium hexafluorophosphate was added.[18] The gummy precipitate formed was triturated with ether. Repeated recrystallizations from absolute ethanol gave a compound of mp 135.5–136.5°.

Anal. Calcd for $C_{17}H_{20}P_2F_6$: C, 51.01; H, 5.03. Found: C, 51.08; H, 5.31.

Reaction of 8 with Sodium Hydroxide.—Sodium hydroxide (1N, 12 ml) was added to a 25-ml flask containing 2.0 g (0.006 mol) of **8**. The resulting suspension (the hexafluorophosphate salt is only slightly soluble in H$_2$O) was refluxed gently for 43 hr. The oxide mixture was worked up as described for the cleavage reaction of **5a** and yielded 0.62 g of a mixture of oxides **6a** and **6b**, bp 120–125° (0.05 mm). Following previously outlined procedures, the oxide mixture was reduced with phenylsilane and quaternized with benzyl bromide to give a 93% yield of salt mixture of mp 150–156°. Comparative nmr analysis using known mixtures of pure **5a** and **5b** showed this to be an approximately equal mixture of the two isomers.

Base-Catalyzed Isomerization of 7a and 7b.—To a 2-ml pear-shaped flask was added 200 mg (733 μmol) of pure **7a**, 15 mg (375 μmol) of sodium hydroxide, and 0.3 ml of water. The reaction mixture was refluxed gently for a period of 16 hr. The ^{31}P nmr spectrum (220 MHz Varian spectrometer) of the reaction mixture provided two peaks of equal area at +95.84 and +96.00 ppm (relative to trimethyl phosphite) as compared with a control solution (100 mg of **7a** in 0.3 ml of water) which showed a single peak at +95.78 ppm.

An identical study was conducted on a mixture of **7a** and **7b** (27% **7a** and 73% **7b**). After base treatment the ^{31}P nmr spectrum showed two signals of equal intensity at +95.94 and +96.09 ppm as compared with the untreated mixture (100 mg salt mixture in 0.3 ml water), which showed signals at +95.86 and +96.01 ppm in the ratio of 27:73, respectively.

Registry No.—*cis*-**5**, 32721-82-7; *trans*-**5**, 32721-83-8; *cis*-**6**, 29587-76-6; *trans*-**6**, 29587-77-7; *cis*-**7**, 32721-23-6; *trans*-**7**, 32721-24-7; **8**, 32721-25-8; *cis*-**15**, 32721-26-9; *trans*-**15**, 32721-27-0.

Acknowledgments.—We wish to express out gratitude to Dr. Frank Lin for determining nmr spectra and to the California Institute of Technology for use of the 220-MHz spectrometer.

Thujopsene Rearrangements. The Ring System *via* Methyl Group Migration[1-3]

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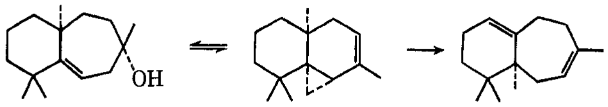
Under mild acid conditions, *cis*-thujopsene rearranges to 1,4,11,11-tetramethylbicyclo[5.4.0]undeca-3,7-diene (**3**). This diene when treated with 0.02 M perchloric acid in refluxing acetic acid rearranges to tricyclic olefin **4** whose structure was proved by degradation and by partial synthesis. This extensive rearrangement which involves a ring closure and two methyl group migrations finds its thermodynamic driving force in the low free energy of the product. The mechanism of the rearrangement is discussed and its relationship to the rearrangement of caryophyllene to neoclovene is noted.

Part A

Under mild acidic conditions, 0.02 M perchloric acid in aqueous dioxane, the equilibrating cyclopropylcarbinyl and homoallyl cations from *cis*-thujopsene (**1**) and widdrol (**2**), respectively, are irreversibly converted by a ring enlargement and angular methyl group migration to the diene **3**.[2] This diene is the major product formed under these acidic conditions and it is stable for long periods, but it is slowly consumed in another reaction. This latter process has now been evaluated by studying the rearrangement of *cis*-thujopsene under more vigorous reaction conditions, namely, 0.02 M perchloric acid in refluxing acetic acid. Under these conditions the rearrangement proceeded past diene **3** and a completely different set of reaction products was formed. Three hydrocarbons in a ratio of 14:4:3 were obtained and in this paper the structure of the major hydrocarbon and its mechanism of formation will be discussed.



2 **1** **3**

Through a series of degradation and synthetic steps, the structure of the major hydrocarbon was established as the tricyclic olefin **4**. A possible pathway for the rearrangement of *cis*-thujopsene (**1**) to this olefin **4** may conveniently involve the diene **3** as an intermediate.

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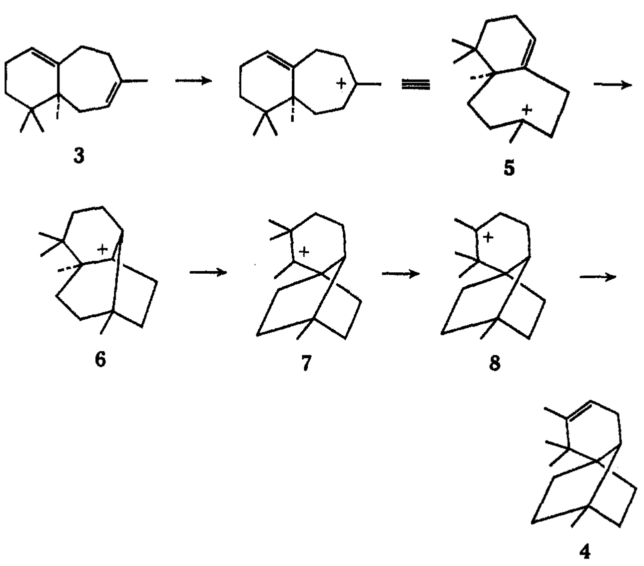
[1] This work was partially supported by Grant GP-8700, National Science Foundation.

[2] For previous papers in this study see (a) W. G. Dauben and L. E. Friedrich, *Tetrahedron Lett.*, 2675 (1964); (b) W. G. Dauben and L. E. Friedrich, *ibid.*, 1735 (1967); (c) W. G. Dauben and E. I. Aoyagi, *Tetrahedron*, **26**, 1249 (1970); (d) W. G. Dauben, L. E. Friedrich, P. Oberhänsli, and E. I. Aoyagi, *J. Org. Chem.*, **37**, 9 (1972).

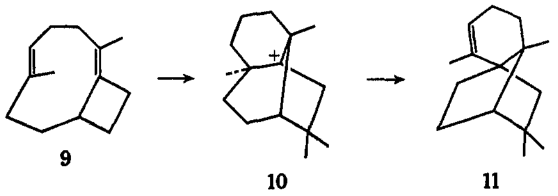
[3] This work appeared in the Abstracts, IUPAC 5th International Symposium on the Chemistry of Natural Products, F-13, London, July 8–13, 1968, p 296.

[4] National Science Foundation Predoctoral Fellow.

Since **3** is not stable indefinitely in acid, the stronger acid conditions used in this present study simply increased the rate of isomerization of **3** to **4**. In this isomerization, protonation of the lesser hindered trisubstituted double bond would generate the tertiary cation **5** which may cyclize to yield the bridgehead cation **6**. This strained cation may undergo a Wagner–Meerwein rearrangement to afford ion **7**, possessing a bicyclo[2.2.1]heptane nucleus and the unstrained tertiary carbonium ion. A subsequent methyl migration would yield the cation **8** which upon loss of a proton would give rise to the tricyclic olefin **4**. The mechanistic pathway employing this series of intermediates does not necessarily provide, step by step, the driving force for the overall rearrangement; the intermediates' only function is to provide a route to the final product whose low free energy content provides the driving force for the overall reaction. Undoubtedly, the major feature of this transformation which accounts for the low free energy content of the tricyclic olefin **4** relative to the diene **3** is the net transformation of one carbon–carbon double bond into two carbon–carbon single bonds. The energy for this conversion may be estimated from the heats of combustion of cyclohexane and *cis*-2-hexene as 18–20 kcal/mol.[5] This decrease in thermochemical energy must compensate for the increased strain of a bicyclo[2.2.1]heptane nucleus, a strain which is estimated to be 14–18 kcal/mol.[6] The additional differential elements of ring strain, nonbonded atom interactions, torsional strain, and entropy considerations cannot be accurately evaluated.



It is of interest to note that the reaction pathway by which caryophyllene (**9**) is thought to be converted under acidic conditions into neoclovene (**11**) is similar to that postulated for the formation of the tricyclic olefin **4**.[7] In caryophyllene, protonation, ring closure, and rearrangement can give a bicyclo[3.2.1]octyl bridgehead cation **10** which upon subsequent rearrangement leads to neoclovene (**11**) with a bicyclo[2.2.1]heptane ring system. In this specific series of transformations, however, the driving force for the reaction should be much larger than in the thujopsene series because of the strain in the four-membered ring of caryophyllene.



Part B

cis-Thujopsene (**1**) was allowed to react with 0.02 *M* perchloric acid in refluxing acetic acid and the major hydrocarbon formed was purified on a preparative scale by chromatography using a silver nitrate impregnated silica gel column.

Quantitative elemental analysis of the major hydrocarbon **4** indicated that the compound was isomeric with the starting *cis*-thujopsene. The nmr spectrum of the hydrocarbon showed one vinyl proton, one vinyl methyl group, and three quaternary methyl groups. The presence of a trisubstituted double bond also was indicated by a maximum at 192 nm,[8] and that this was the only unsaturated linkage in the molecule was indicated by a molar extinction coefficient of 8860. Therefore, since the starting thujopsene was tricyclic with one double bond, this new olefin **4** must also be tricyclic.

Hydroboration of the tricyclic olefin **4** gave alcohol **12**, which was oxidized to the tricyclic ketone **13** with Jones reagent. Alumina chromatography of this ketone gave an isomeric ketone **14**, indicating that hydroboration of the olefin **4** gave an alcohol with an axially oriented methyl group at C-3. The carbonyl absorption in the infrared spectra of ketone **13** and **14** (1713 and 1710 cm^{-1}) established that the double bond of the olefin **4** was most likely located endocyclic in a six-membered ring. Furthermore, a one-proton quartet at δ 2.67 and a two-proton multiplet at δ 1.98–2.31 in the nmr spectrum of the ketone **14** tentatively identify C-2 as a quaternary carbon atom and C-5 as a methylene group.

It was of importance to establish that the alumina chromatography of ketone **13** induced only epimerization and not a skeletal rearrangement. Therefore, the ketone **14** was reduced with $LiAlH_4$ to alcohol **15**. This alcohol was identical with the minor alcohol obtained from the $LiAlH_4$ reduction of epoxide **16**, prepared from the reaction of olefin **4** with *m*-chloroperbenzoic acid. The major alcohol **17** of this latter reaction was formed by the 1,2-diequatorial opening of the oxirane ring, a result often found with epoxides which are of the secondary–tertiary type.[9] These positional and stereochemical assignments were confirmed by reduction of ketone **13** with $LiAlH_4$ to yield the hydroboration alcohol **12** and a new equatorial tricyclic alcohol **18** in 48 and 33% yield, respectively. Finally, oxidation of alcohol **15** with Jones reagent gave the more stable ketone **14**. The selective formation of alcohol **12** and epoxide **16** from hydroboration and from epoxidation

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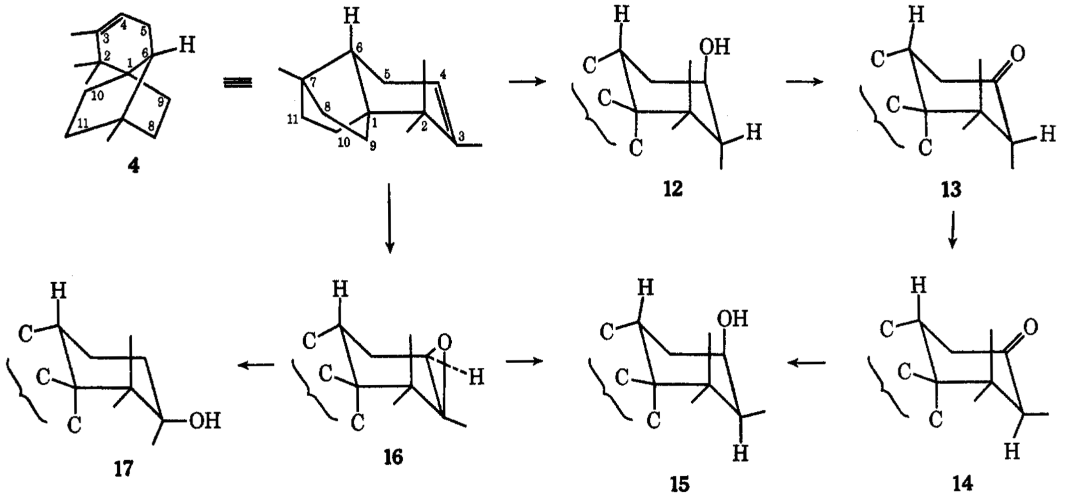
[5] F. D. Rossini, K. S. Pitzer, R. C. Arnett, R. M. Braun, and G. C. Pimentel, "Selective Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, pp 451, 455.

[6] K. B. Wiberg, private communication.

[7] W. Parker, R. A. Raphael, and J. S. Roberts, *J. Chem. Soc. C*, 2634 (1969).

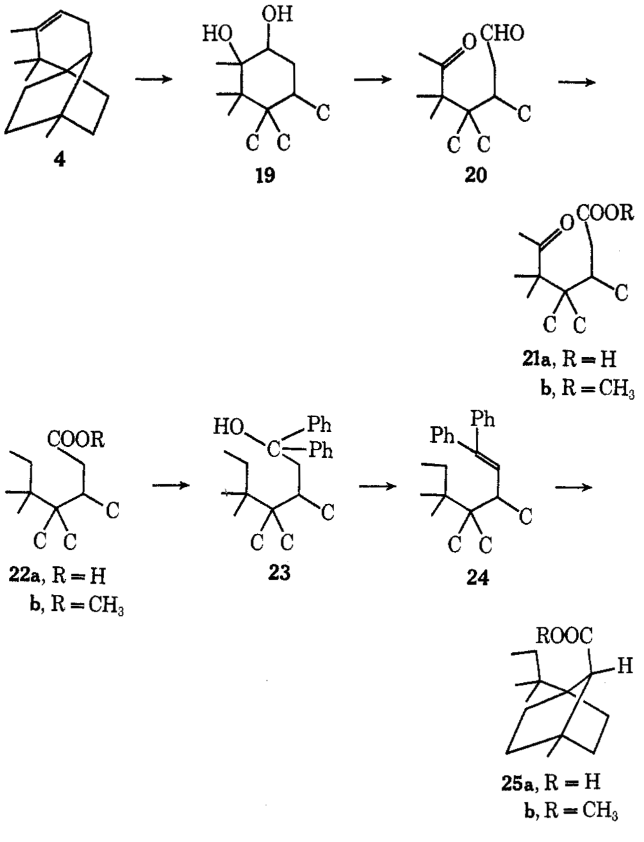
[8] R. A. Micheli and T. H. Applewhite, *J. Org. Chem.*, **27**, 345 (1962).

[9] C. Djerassi, "Steroid Reactions," Holden-Day, San Francisco, Calif., 1963, p 636; N. A. LeBel and G. G. Ecke, *J. Org. Chem.*, **30**, 4316 (1965).



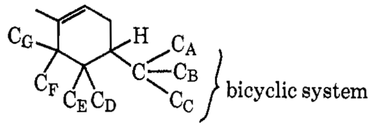
established that the C-8,9-dimethano bridge of the tricyclic hydrocarbon hinders the bottom side of the double bond more than the pseudoaxially oriented methyl group on C-2 hinders the topside of the double bond.

With the substitution and the surroundings of the double bond established, the unsaturated linkage was cleaved *via* the formation of the diol **19** with osmium tetroxide and scission to keto aldehyde **20** with lead tetraacetate. The nmr spectrum of **20** indicated the presence of a methyl ketone (3 H, singlet, δ 2.04) confirming the presence of a vinyl methyl group in the olefin **4**. Also, the one-proton aldehyde triplet (J = 1.5 Hz, δ 9.63) confirmed the presence of two protons on C-5.



The keto aldehyde **20** was oxidized to the keto acid **21a** with potassium permanganate. This keto acid and its methyl ester **21b** failed to react with 2,4-dinitrophenylhydrazine and with trifluoroperacetic acid. This lack of reactivity is characteristic of highly hindered ketones[10] and is in agreement with the placement of the *gem*-dimethyl group at C-2. The keto ester **21b** was reduced under forcing Wolff–Kishner conditions[11] and the acid **22a** after conversion to its methyl ester **22b** was degraded according to the Barbier–Wieland method. Treatment of **22b** with phenylmagnesium bromide yielded the carbinol **23** which was dehydrated to give the diphenyl olefin **24**. The nmr spectrum of **24** showed a one vinyl proton doublet at δ 6.03 coupled to another one-proton doublet at δ 2.07 (J = 11 Hz). The absence of further splitting of the allylic proton at δ 2.07 indicated that the neighboring carbons must be quaternary. Oxidation of **24** gave bicyclic acid **25a**.

Summarizing the data available, a partial structure **26** can be formulated. In this structure, three of the unallocated carbon atoms labeled A–G must be methyl groups, two of which are geminal. The location of these latter two methyl groups was achieved by examination of the changes in chemical shifts of the methyl groups with the various chemical transformations. From the data in Table I, it is seen that the presence of a carbonyl function at C-3 (**21a**, **21b**, **27b**) causes two methyl groups to resonate at an average field of δ 1.19. Removal of the oxygen function (**22a**, **22b**) shifts the average absorption of these two methyl groups upfield by an average of δ 0.3. Such a large shift is commen-



26

TABLE I

CHEMICAL SHIFTS OF METHYL GROUPS

Compd	Methyl shifts, δ
21a	1.19, 1.19, 0.93
21b	1.15, 1.15, 0.88
27b	1.27, 1.17, 0.88
22a	0.94, 0.88, 0.83
22b	0.88, 0.88, 0.88

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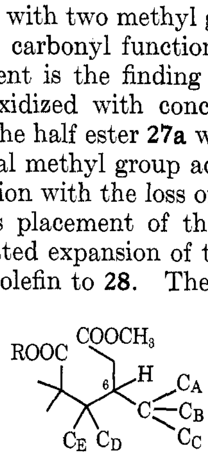
[10] G. Büchi, R. E. Erickson, and H. Wakabayashi, *J. Amer. Chem. Soc.*, **83**, 927 (1961).

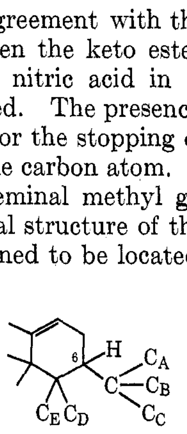
[11] D. H. R. Barton, D. A. Ives, and B. R. Thomas, *J. Chem. Soc.*, 2056 (1955).

surate with two methyl groups substituted at C-2, next to the carbonyl function. In agreement with this assignment is the finding that when the keto ester **21b** was oxidized with concentrated nitric acid in acetic acid, the half ester **27a** was formed. The presence of a geminal methyl group accounts for the stopping of the oxidation with the loss of only one carbon atom.

This placement of the two geminal methyl groups permitted expansion of the partial structure of the tricyclic olefin to **28**. There remained to be located two methylene groups and a quaternary methyl group. If the logical assumption is made that no cyclopropane ring would remain under the strong acidic conditions utilized for the formation of the tricyclic olefin **4**, only the structures **29–31** can be formulated for this hydrocarbon. The evidence required to differentiate these three structures was provided by bromination followed by dehydrobromination of the tricyclic olefin to give the optically active conjugated diene **32**, $[\alpha]_D$ −73°.



27a, R = H
b, R = CH$_3$



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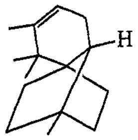

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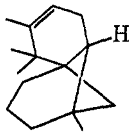

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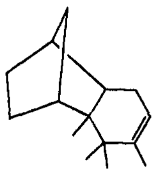

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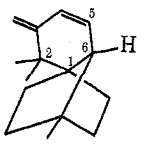

32

The structure and placement of this new chromophore was readily established by its spectral properties. When the diene was allowed to react with potassium *tert*-butoxide in dimethyl sulfoxide, the starting material was recovered but was partially racemized, $[\alpha]_D$ −28°.[12] To account for these facts, in **29** carbons 1, 2, and 6 must be in a potential symmetry plane of the molecule whereas C-5 is not in the plane. The base-catalyzed removal of the hydrogen on C-6 to yield a carbanion would provide a mechanism to racemize diene **32**. These symmetry demands would not be met by dienes derived from **30** and **31** since base treatment of them would yield only starting material unchanged in optical purity or an isomer, not a mirror image. Thus, compilation of all of these data permits structure **29** to be assigned to the tricyclic olefin **4**.

In view of the extensive structural changes undergone in this acid-catalyzed rearrangement of thujopsene, an unequivocal synthesis of the degradation acid **25a** was performed. Birch reduction of the known *p*-(*tert*-amyl)toluene (**33**)[13] gave **34** which upon reaction with potassium *tert*-butoxide in dimethyl sulfoxide[14] gave a 86:14 mixture of conjugated diene **35** and nonconjugated diene **34**. Distillation of the crude reaction product gave material of 90% purity, a purity sufficient to permit its use in the Diels–Alder reaction with maleic anhydride. The adduct **36** was obtained in high yield; the anhydride was hydrogenated and hydrolyzed to yield the cis diacid **37**. Reaction of **37** with lead tetraacetate under the Grob oxidative bisdecarboxylation conditions gave olefin **38** in 65% yield. The two vinyl protons of **38** exhibited an AB quartet pattern in the nmr spectrum at δ 6.13 and 5.88 (J = 8 Hz).

Hydroboration of olefin **38** gave the two alcohols **39** and **40**. A minor (~10%) product of the reaction was a polar product; this material is postulated to be the boronic acid **45** because its infrared spectrum shows oxygen–hydrogen stretching absorptions and a strong band at 1365 cm^{-1}, characteristic of oxygen–boron stretching absorption.[15] Upon standing, this polar major product no longer exhibited the oxygen–hydrogen absorptions in the infrared. These data are consistent with the known facile trimerization of a boronic acid to a boroxine (**46**).[16] This new product when allowed to react with excess alkaline hydrogen peroxide under reflux in tetrahydrofuran solution gave the major alcohol **40** in good yield. The structure assigned to the major alcohol is in analogy with the finding that the major product from the hydroboration of 3,3-dimethyl-1-cyclohexene is the lesser hindered 3,3-dimethylcyclohexan-1-ol.

The mixture of alcohols **39** and **40**, as well as each individual alcohol, was oxidized with Jones reagent to yield ketones **41** and **42**. Each ketone showed an nmr resonance attributable to the methylene protons adjacent to the carbonyl group. The methylene hydrogens of the major ketone **42** absorb at higher field (δ 1.95) than the hydrogens of the minor ketone **41** (δ 2.07). It is to be expected that the *tert*-amyl group would be more shielding than a methyl group,[17] and the structure assignments are in agreement with this postulate.

Both ketones **41** and **42** upon oxidation by selenium dioxide in *o*-xylene gave the diketone **43a**. Upon reaction with *p*-toluenesulfonylhydrazine, the diketone yielded a keto tosylhydrazone **43b** which in chloroform solution was filtered through basic alumina to give the crystalline diazo ketone **43c**. Irradiation through Corex of an aqueous tetrahydrofuran solution of **43c** gave an almost quantitative yield of ketene **44**. The ketene was converted into the bicyclic acid **25a** upon reaction with aqueous acid. The acid and its methyl ester were identical with the bicyclic acid and methyl ester obtained from the degradation of the tricyclic olefin **4**.

Several properties of this acid warrant comment.

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[12] The incomplete racemization may be a consequence of the excessive strain in the bond angle C-1:C-6:C-7 which retards the formation of a trigonal carbon at C-6 (see J. P. Schaefer and D. S. Winberg, *J. Org. Chem.*, **30**, 2635 (1961), and references cited therein).

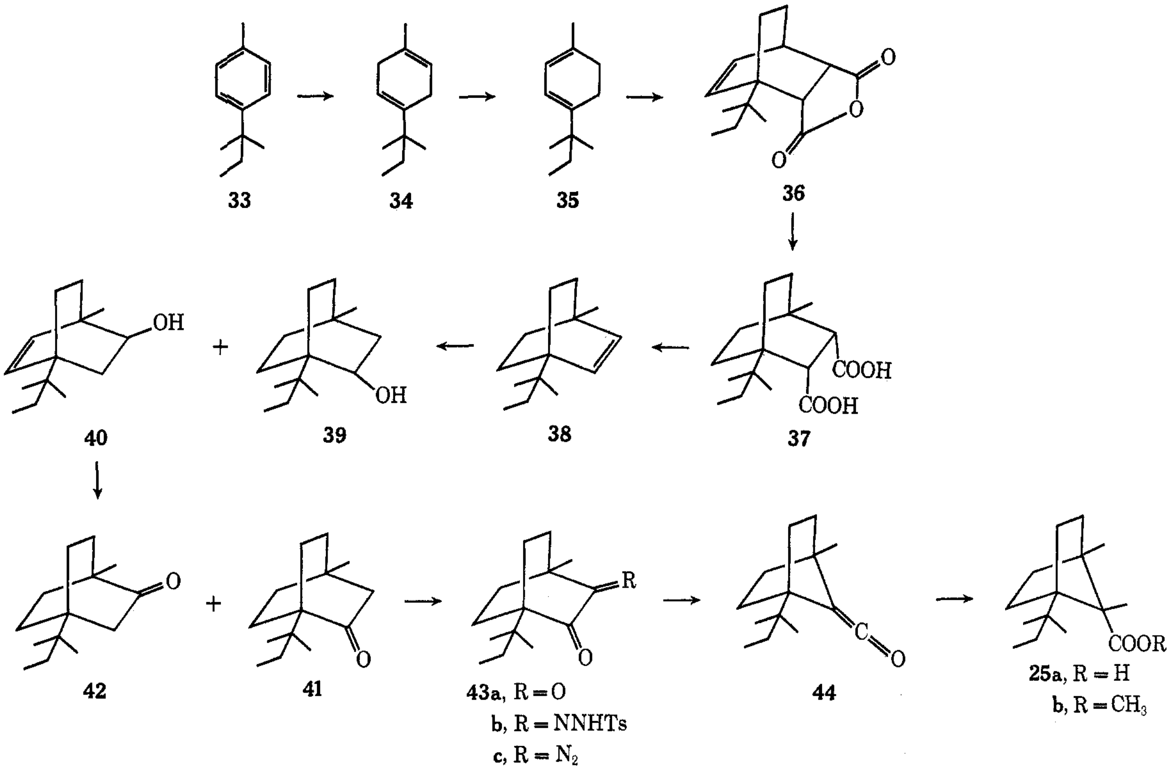
[13] G. W. Hearne, T. W. Evans, V. W. Buls, and C. G. Schwarzer, *Ind. Eng. Chem.*, **47**, 2311 (1955).

[14] W. G. Dauben and P. Oberhänsli, *J. Org. Chem.*, **31**, 315 (1966).

[15] C. N. R. Rao, "Chemical Applications in Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 283.

[16] M. F. Lappert, *Chem. Rev.*, **56**, 959 (1956).

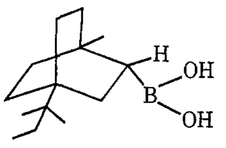
[17] In a related bicyclic system, it has been reported that bridgehead alkyl substituents of several 7-oxabicyclo[2.2.1]heptanes diamagnetically shield neighboring protons; see S. Seltzer, *J. Amer. Chem. Soc.*, **87**, 1534 (1965).



33 → 34 → 35 → 36 → 37 → 38 → 39 + 40; 40 → 42 + 41 → 43 → 44 → 25

43a, $R = O$
b, $R = NNHTs$
c, $R = N_2$

25a, $R = H$
b, $R = CH_3$



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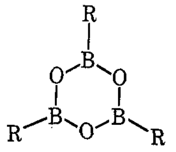

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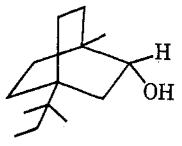

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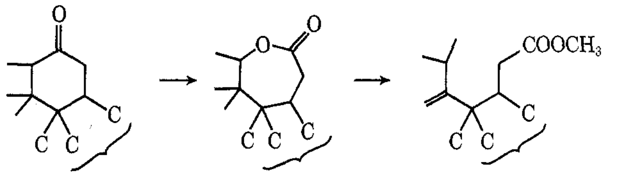
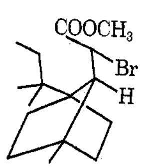
The acid could not be extracted from an ethereal solution with half-saturated aqueous potassium bicarbonate solution. The related methyl ester **25b** could not be hydrolyzed with 1.8 *M* potassium hydroxide in 90% aqueous methanol at reflux temperature in 7 hr. Also, the ketene **44** was stable to 1 *M* aqueous potassium hydroxide at room temperature. In contrast, 7-norbornylcarboxylic acid and 7-norbornylketene are much more reactive compounds.[18] These and other facts suggest that the bridgehead alkyl substituents of **25a** abnormally hinder the vicinity of the functional group. This conclusion is confirmed by the low acidity of acid **18a**, $pK^*_{MCS} = 8.44$.[19,20] Secondary aliphatic carboxylic acids are generally more acidic by a factor of ten than the value found for **25a**.[21] This abnormal hindrance by the bridgehead substituents undoubtedly also causes the experimental difficulties found in the hydroboration reaction.

In the course of these degradational studies, a variety of methods was studied in order to ascertain the best way to cleave the unsaturated ring. Of these many reactions the Baeyer–Villiger oxidation of ketone **14** is worthy of special mention. The lactone **47** formed by reaction of **14** with trifluoroperacetic acid was hydrolyzed on an alumina column to its related hydroxy acid but when the column was washed with water a mixture of both the hydroxy acid and the lactone **47** was obtained. Treatment of the lactone with a solution of boron trifluoride etherate in methanol yielded the rearranged, dehydrated ester **48** whose structure was readily established by its nmr spectrum.

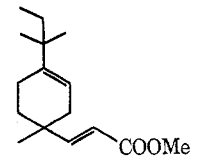


14 → 47 → 48

Finally, it is of interest to note the ease of rearrangement of the bicyclo[2.2.1]heptane system. The bromo ester **49**, a 5:3 diastereomeric mixture, was prepared from the acid **22a** in the standard fashion. Dehydrohalogenation of **49** in quinoline gave the unexpected fragmentation product **50** which was characterized on the basis of spectral data. Since the material was optically inactive, the overall elimination of the hydrogen bromide and the ring scission appears to be a stepwise process rather than a concerted fragmentation reaction.[22]



49



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[18] P. Yates and R. J. Crandall, *J. Amer. Chem. Soc.*, **88**, 1292 (1966).

[19] The acidity of acid **18a** was kindly measured by Professor W. Simon, Eidg. Techn. Hochschule, Zurich.

[20] P. F. Sommer, V. P. Arya, and W. Simon, *Tetrahedron Lett.*, 18 (1960); P. F. Sommer, C. Pascual, V. P. Arya, and W. Simon, *Helv. Chim. Acta*, **46**, 1734 (1963).

[21] P. F. Sommer and W. Simon, "Scheinbare Dissociations Konstanten," Band II, Juris-Verlag, Zurich, 1961.

[22] It has been reported by J. Martin, W. Parker, and R. H. Raphael [*J. Chem. Soc. C*, 348 (1967)] that attempts to dehydrate the β-hydroxy ester found in the Reformatsky reaction with 1,5-dimethylbicyclo[3.3.1]nonan-9-one gave the expected unsaturated ester in only 3% yield.

This abnormal dehydrohalogenation reaction was further investigated using α-bromobicyclo[2.2.1]heptane-7-acetic acid and its methyl ester. Using boiling quinoline, conditions under which the desired α,β-unsaturated ester was shown to be stable, the bromo ester yielded only a small amount of reductively debrominated ester; the major amount of starting material was destroyed. Using potassium *tert*-butoxide in *tert*-butyl alcohol, again no dehydrobromination occurred, the only reaction being transesterification to give the *tert*-butyl ester. When the bromo acid was treated with potassium *tert*-butoxide in toluene, a small yield of unsaturated acid was obtained. However, when these conditions were used with the bromo acid found in the degradation study, again only decomposition occurred.

Experimental Section

Infrared spectra were run either with a Perkin-Elmer Model 137 or Model 237 spectrometer. Ultraviolet spectra were recorded with either a Perkin-Elmer Model 202 spectrometer or, when necessary, a nitrogen-flushed Beckman Model DK2-A spectrometer. Nuclear magnetic resonance spectra were obtained with a Varian Model A-60 spectrometer. Optical rotations at the sodium D line were calculated from the rotations at 546 and 578 nm with the Drude equation; these latter rotations were measured with a Zeiss LEP-A2 photoelectric polarimeter with a 10-cm cell length. Mass spectra were obtained with a modified C.E.C. 21-103C mass spectrometer at the University of California, Berkeley.

Melting points were measured with a Büchi Schmelzpunktbestimmungsapparat; they were obtained in unevacuated melting point tubes and are uncorrected. Boiling points are uncorrected. Vapor phase chromatographies were conducted on a Wilkins Aerograph Model A90-P with a helium carrier gas flow rate between 50 and 150 ml/min, depending on the need. Combustion analyses and molecular weight determinations were performed by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley.

All extractions were washed with acid or base until neutral, water, and saturated salt solution, and dried over anhydrous sodium sulfate. The solvent was removed either by distillation at reduced pressure or rotary evaporation. All infrared spectra and nmr spectra were taken in CCl_4 unless otherwise noted.

Perchloric Acid–Acetic Acid Treatment of *cis*-Thujopsene.—A mixture of 65.0 g (0.318 mol) of natural *cis*-thujopsene, 500 ml of glacial acetic acid, and 1.00 ml of 70% aqueous perchloric acid was heated under reflux for 48 hr under an atmosphere of nitrogen in the absence of light. The dark brown reaction mixture was diluted with water and extracted with hexane to yield 64.7 g of a brown, fluid oil. Glpc analysis of the crude product, using 3-keto-10-methyl-Δ^4-octalone as an internal standard, indicated that the major product of the reaction was formed in 37% yield (20% DEGS, firebrick, 150°, 5 ft × 0.25 in.) which composed *ca.* 70% of the area of the chromatogram. Infrared and nmr spectral analyses of the crude product did not indicate the formation of acetate or alcoholic products. Extensive polymerization of the product was reduced by a rapid flash distillation of the mixture preceding the slow spinning band distillation. Nevertheless, the major product was not separated from other isomeric impurities in the mixture.

The major product was purified best on a preparative scale by chromatography. Accordingly, 1.00 g of the crude reaction product was chromatographed on 30.0 g of 22% silver nitrate impregnated on silica gel (height to diameter 9.7). The major product was eluted by hexane in fractions 6 through 9 (23 ml/fraction), yield 262 mg, 88% pure (23%). A pure sample of the tricyclic olefin **4** was obtained by preparative glpc (20% DEGS, firebrick, 150°, 5 ft × 0.25 in.): bp 112° (9 mm); $[\alpha]^{23}\text{D}$ −46° (*c* 1.41, $CHCl_3$); uv max (cyclohexane) 192 nm (ε 8860); nmr δ 5.20 (m, 1), 1.67 (sharp multiplet, 3), 1.00 (s, 3), 0.97 (s, 3), 0.87 (s, 3).

Anal. Calcd for $C_{15}H_{24}$ (204.34): C, 88.16; H, 11.84. Found: C, 87.94; H, 11.64.

Hydroboration of Tricyclic Olefin 4.—A solution of 10.0 g of tricyclic olefin **4** (70% pure, 0.034 mol) in 125 ml of tetrahydrofuran, cooled at 0° in an atmosphere of nitrogen, was allowed to react with 0.084 mol of diborane. The reaction mixture allowed to warm to room temperature and stand for an additional 5 hr; then 32 ml of 3 *M* aqueous sodium hydroxide and 32 ml of 30% aqueous hydrogen peroxide were added. The mixture was stirred at 40° for 1 hr, and processed in the standard fashion to yield 10.90 g of residual colorless oil, which was chromatographed on 200 g of Woelm neutral alumina (activity II). Elution with 650 ml of hexane yielded 6.8 g of a fluid oil. The remainder of the product was eluted with 400 ml of diethyl ether to yield 4.0 g of a viscous oil which slowly solidified. The first fraction was rechromatographed to obtain a total of 6.8 g of a waxy solid (90%). Analysis of the original hexane fraction by glpc (20% DEGS, Chromosorb P, 160°, 5 ft × 0.25 in.) indicated that the impurities in the starting material did not react with diborane. An analytical sample of the tricyclic alcohol **12** was prepared by slow recrystallization of a portion of the product from hexane: mp 67–70°; $[\alpha]^{23}\text{D}$ +3° (*c* 6.81, $CHCl_3$); uv at 210 nm (cyclohexane) (ε 75); nmr δ 3.96 (broad multiplet, 1), 1.17 (s, 3), 1.01 (d, 3, *J* = 7 Hz), 0.98 (s, 3), 0.86 (s, 3).

Anal. Calcd for $C_{15}H_{26}O$ (222.36): C, 81.02; H, 11.79. Found: C, 81.26; H, 11.57.

Oxidation of Tricyclic Alcohol 12.—A solution of 4.04 g (0.018 mol) of crude tricyclic alcohol **12** and 125 ml of acetone was cooled to −20° and 5.0 ml (1.1 equiv) of Jones reagent was slowly added. The mixture was stirred for 15 min, 2 ml of isopropyl alcohol was added, and then the mixture was worked up to yield the crude tricyclic ketone **13**: 3.90 g (98%); $[\alpha]^{23}\text{D}$ −110° (*c* 7.02, $CHCl_3$); ir 1713 cm^{-1}; nmr δ 2.00–2.37 (m, 3), 1.08 (d, 3, *J* = 7 Hz), 1.03 (s, 3), 0.98 (s, 3), 0.83 (s, 3).

A 2,4-dinitrophenylhydrazone derivative was prepared and recrystallized from methyl alcohol, orange crystals, mp 172–183°.

Anal. Calcd for $C_{21}H_{28}N_4O_4$ (400.46): C, 62.98; H, 7.05; N, 13.99. Found: C, 62.80; H, 6.98; N, 13.90.

The crude tricyclic ketone **13** was filtered through 190 g of Woelm neutral alumina (activity II) with benzene to yield 3.33 g (84%) of tricyclic ketone **14** which solidified after several weeks. A small portion of the material was purified by preparative glpc (20% DEGS, Chromosorb P, 160°, 5 ft × 0.25 in.): mp 40°; $[\alpha]^{23}\text{D}$ −52° (*c* 7.07, $CHCl_3$); ir 1710 cm^{-1}; nmr δ 2.67 (q, 1, *J* = 7 Hz), 1.98–2.31 (m, 2), 0.96 (s, 3), 0.89 (d, 3, *J* = 7 Hz), 0.88 (s, 3), 0.78 (s, 3).

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.54; H, 10.91.

A 2,4-dinitrophenylhydrazone derivative was prepared, yellow solid, mp 180.0–180.5°.

Anal. Calcd for $C_{21}H_{28}N_4O_4$: C, 62.98; H, 7.05; N, 13.99. Found: C, 63.07; H, 6.76; N, 14.28.

Lithium Aluminum Hydride Reduction of Tricyclic Ketone 13.—A mixture of 300 mg (1.37 mmol) of crude tricyclic ketone **13**, 1.02 g (27 mmol) of lithium aluminum hydride, and 100 ml of diethyl ether was stirred for 1.5 hr at room temperature; 266 mg of the crude product was chromatographed on 13 g of Woelm neutral alumina (activity II). Benzene (68 ml) eluted 145 mg (48%) of a white solid. An infrared spectrum of the material was identical with the spectrum of tricyclic alcohol **12**. An additional 86 ml of benzene and 60 ml of benzene–diethyl ether (95:5) eluted 101 mg (33%) of tricyclic alcohol **18**, mp 123–127°. A small portion of the alcohol was recrystallized from hexane: mp 131–132°; $[\alpha]^{23}\text{D}$ −5° (*c* 2.84, $CHCl_3$); nmr δ 3.75–4.20 (broad m, 1) 1.03 (s, 3), 1.01 (d, 3, *J* = 7 Hz), 0.98 (s, 3), 0.89 (s, 3).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.20; H, 11.50.

Lithium Aluminum Hydride Reduction of Tricyclic Ketone 14.—A mixture of 109 mg (0.49 mmol) of crude tricyclic ketone **14**, 100 mg (2.64 mmol) of lithium aluminum hydride, and 15 ml of diethyl ether was stirred for 13 hr at room temperature; 115 mg (100%) of the crude product was filtered through a small amount of Woelm neutral alumina (activity II) in diethyl ether to yield tricyclic alcohol **15**: $[\alpha]^{23}\text{D}$ −5° (*c* 2.07, $CHCl_3$); nmr δ 3.79 (m, 1), 1.00 (d, 3, *J* = 7 Hz), 0.96 (s, 6), 0.75 (s, 3).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.26; H, 11.57.

Treatment of Tricyclic Olefin 4 with *m*-Chloroperbenzoic Acid.—A solution of 100 mg (0.49 mmol) of 85% *m*-chloroperbenzoic acid in 3 ml of chloroform was slowly added to a solution of 100 mg (0.49 mmol) of greater than 95% pure tricyclic olefin **4** in 2.0 ml of chloroform at 0°. After 13 hr at 0°, the mixture was poured into half-saturated aqueous potassium bicarbonate and processed to give a residual light yellow oil, 121 mg, which was filtered through 3 g of Woelm neutral alumina (activity II) with hexane to yield 106 mg (99%) of tricyclic epoxide **16**: $[\alpha]^{23}\text{D}$ −42° (*c* 0.4367, $CHCl_3$); nmr δ 2.90 (m, 1), 1.16 (s, 3), 0.94 (s, 6), 0.88 (s, 3).

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.70; H, 10.88.

Lithium Aluminum Hydride Reduction of Tricyclic Epoxide 16.—A mixture of 3.50 g (15.9 mmol) of tricyclic epoxide **16**, 1.498 g (39.4 mmol) of lithium aluminum hydride, and 125 ml of ethylene glycol dimethyl ether was heated under reflux for 49.5 hr under nitrogen. The mixture was allowed to react for an additional three days at room temperature. After work-up, 3.67 g of a residual oil was chromatographed on 180 g of Woelm neutral alumina (activity II). Hexane (1115 ml) eluted 457 mg of unidentified material which was not investigated. Hexane–benzene (330 ml, increasingly greater amounts of benzene) and finally benzene (1210 ml) eluted two alcohols. Infrared and nmr spectra of the first alcohol, 650 mg (18%), were identical with the spectra of tricyclic alcohol **15**. Jones oxidation of this material afforded tricyclic ketone **14**, as determined by infrared and nmr spectroscopy. The second alcohol solidified after several weeks to yield 1.432 g (41%) of tricyclic alcohol **17**: mp 46–50°; $[\alpha]^{23}\text{D}$ +9° (*c* 2.69, $CHCl_3$); nmr δ 1.33 (s, 3), 1.04 (s, 3), 0.95 (s, 3), 0.85 (s, 3).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.89; H, 11.62.

Treatment of Tricyclic Olefin 4 with Osmium Tetroxide.—A mixture of 3.34 g (16.3 mmol) of 90% pure tricyclic olefin **4**, 175 ml of diethyl ether, 4.17 ml of pyridine, and 4.24 g (16.7 mmol) of osmium tetroxide was allowed to react at room temperature in the absence of light for 1 month (later it was found, 1 week was sufficient); the brown tacky crude osmylate was dissolved in 175 ml of diethyl ether, and reduced with 2.40 g (63 mmol) of lithium aluminum hydride (20 hr). The reaction mixture yielded 4.53 g of a viscous yellow oil which was chromatographed on 175 g of Woelm neutral alumina (activity II). Elution with benzene–diethyl ether (increasingly greater amounts of diethyl ether) yielded 2.13 g of an unidentified oil: nmr δ 4.83 (broad singlet), 1.61 (narrow multiplet), 0.97 (s), 0.92 (s). The tricyclic diol **19** was eluted with pure diethyl ether, yield 2.00 g (51%). A small portion of the product was recrystallized from carbon tetrachloride: mp 124–125°; $[\alpha]^{23}\text{D}$ +5° (*c* 2.10, $CHCl_3$); nmr δ 3.55 (broad m, 1), 1.21 (s, 3), 0.97 (s, 3), 0.94 (s, 3), 0.91 (s, 3).

Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.41; H, 10.76.

Treatment of Tricyclic Diol 19 with Lead Tetraacetate.—A mixture of 1.944 g (8.2 mmol) of tricyclic diol **19**, 175 ml of glacial acetic acid, and 8.80 g (19.80 mmol) of lead tetraacetate was stirred under a nitrogen atmosphere at room temperature for 40 hr. The solution was diluted with water and extracted with four portions of diethyl ether. The combined ethereal solutions were processed in the standard manner to yield 1.88 g (98%) of crude bicyclic keto aldehyde **20**. A small portion of this material was rapidly oxidized overnight at room temperature in the atmosphere to bicyclic keto acid **21a**. Therefore, the crude keto aldehyde was used directly in the next experiment: ir 2713, 1730, 1703 cm^{-1}; nmr δ 9.63 (t, 1, *J* = 1.5 Hz), 2.04 (s, 3), 1.13 (s, 6), 0.88 (s, 3).

Oxidation of Bicyclic Keto Aldehyde 20.—A solution of 2.280 g (14.4 mmol) of potassium permanganate in 30 ml of water was slowly added to a solution of 1.80 g (7.6 mmol) of crude bicyclic keto aldehyde **20** in 200 ml of acetone. The mixture was stirred for 3 hr at room temperature, diluted with water containing 2.0 ml of concentrated aqueous hydrochloric acid, extracted with ether, and processed to yield 1.08 g (53% yield from tricyclic diol **19**) of bicyclic keto acid **21a**. A portion of the material was recrystallized twice from hexane: mp 104–105°; $[\alpha]^{23}\text{D}$ +4° (*c* 4.56, $CHCl_3$); ir 1706 cm^{-1}; nmr δ 2.08 (s, 3), 1.19 (s, 6), 0.97 (s, 3).

Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.50; H, 9.35.

The product failed to react with 2,4-dinitrophenylhydrazine.

Wolff–Kishner Reduction of Bicyclic Keto Acid 21a.—A solution of 249 mg (10.8 mg-atoms) of sodium metal in 5 ml of distilled diethylene glycol was added to 2 ml (63 mmol) of anhydrous hydrazine[11,23] and 300 mg (1.193 mmol) of bicyclic keto acid **21a** and heated under reflux for 35 hr. The excess hydrazine was distilled from the solution until the temperature in the reaction flask reached 200°. The solution was heated under reflux for 27 hr, and worked up to yield 275 mg (98%) of bicyclic acid **22a** which slowly solidified. A small portion of the material was recrystallized twice from hexane: mp 87–88°; $[\alpha]^{23}\text{D}$ −7° (*c* 6.15, $CHCl_3$); ir 1709 cm^{-1}; nmr δ 2.15–2.75 (m, 2), 0.94 (s, 3), 0.88 (s, 3), 0.84 (s, 3), 0.83 (broad t, 3, *J* = 7 Hz).

Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.37; H, 10.63.

The acid was esterified with diazomethane and the ester was chromatographed on Woelm neutral alumina (activity II). Elution with hexane yielded the pure ester **22b**: $[\alpha]^{23}\text{D}$ −5° (*c* 8.13, $CHCl_3$); ir 1738 cm^{-1}; nmr δ 3.59 (s, 3), 2.13–2.70 (m, 2), 0.88 (s, 9), 0.83 (broad t, 3, *J* = 7 Hz).

Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 75.96; H, 10.88.

Treatment of Bicyclic Ester 22b with Phenylmagnesium Bromide. To a solution of 86 mmol of phenylmagnesium bromide was added 2.20 g (8.71 mmol) of bicyclic ester **22b** in 25 ml of dry ether. The solution was heated under reflux for 9 hr and allowed to react at room temperature for an additional 12 hr. The mixture was processed in the standard fashion and the crude 3.99 g of a yellow oil was chromatographed on 123 g of Woelm neutral alumina (activity II). Hexane eluted 554 mg of unreacted ester. Hexane–diethyl ether (85:15) eluted 2.239 g of the crude diphenylcarbinol **23** which was rechromatographed on 46 g of Woelm neutral alumina (activity II) to yield a total of 989 mg (45%) of unreacted ester and 1.390 g (42%) of crude diphenylcarbinol **23**. The unreacted ester was allowed to react with an ethereal solution of 85.5 mmol of phenylmagnesium bromide as previously described. Isolation and alumina chromatography yielded a total of 2.001 g (61%) of crude liquid diphenylcarbinol **23**: ir 3597, 3044, 1600, 699 cm^{-1}; nmr δ 7.00–7.57 (m, 10), 0.78 (s, 3), 0.73 (s, 3), 0.48 (s, 3).

Anal. Calcd for $C_{27}H_{36}O$: C, 86.11; H, 9.64. Found: C, 84.80; H, 9.31.

Dehydration of Diphenylcarbinol 23.—A mixture of 1.75 g (4.7 mmol) of diphenylcarbinol **23**, 38 ml of water, and 190 ml of acetic acid was heated at 90° on a steam bath for 2.5 hr, and worked up in the usual way to yield 1.55 g of a yellow oil. The material was chromatographed on 85 g of Woelm neutral alumina (activity I) and the diphenyl olefin **24** was eluted with hexane–diethyl ether (95:5): yield 1.418 g (74%); $[\alpha]^{23}\text{D}$ +202° (*c* 2.85, $CHCl_3$); nmr δ 6.99–7.53 (m, 10), 6.03 (d, 1, *J* = 11 Hz), 2.07 (d, 1, *J* = 11 Hz), 1.03 (s, 3), 0.83 (s, 3), 0.78 (s, 3), 0.75 (broad t, 3, *J* = 7 Hz).

Anal. Calcd for $C_{27}H_{34}$: C, 90.44; H, 9.56. Found: C, 90.22; H, 9.77.

Treatment of Diphenyl Olefin 24 with Ruthenium Tetroxide.—A mixture of 1.57 g of sodium metaperiodate, 121 mg (0.905 mmol) of ruthenium dioxide, and 30 ml of water was stirred at 0° for 30 min. An additional 1.60 g of sodium metaperiodate was added to the mixture, followed by the dropwise addition of 1.406 g (3.92 mmol) of diphenyl olefin **24** dissolved in 76 ml of cold acetone (distilled from potassium permanganate). A black precipitate formed immediately. During the next 9 hr at room temperature with vigorous stirring, a total of 12.80 g of sodium metaperiodate was added in 1.60-g portions in order to remove the black precipitate whenever it appeared. The excess ruthenium tetroxide was destroyed by the addition of 16 ml of isopropyl alcohol and the mixture was placed in the refrigerator overnight. The mixture was added to an aqueous sodium chloride solution containing 1.0 ml of concentrated aqueous hydrochloric acid and extracted with ether. The combined ethereal extracts were washed with water and half-saturated aqueous potassium bicarbonate. The basic water solution was washed with diethyl ether, acidified with concentrated aqueous hydrochloric acid, and extracted with four portions of diethyl ether. The combined ethereal extracts were worked up to yield 238 mg of benzoic acid. The original base-washed ethereal solution was washed twice with water and dried, and the solvent was removed under reduced pressure. This material was dissolved in hexane and extracted with 50 ml of 1 *M* aqueous sodium hydroxide and twice with water. The aqueous extracts were combined, washed with hexane, acidified with concentrated aqueous hydrochloric acid, and extracted with four portions of diethyl ether. The combined ethereal solutions were processed to yield 798 mg (91%) of crude bicyclic acid **25a**: $[\alpha]^{23}\text{D}$ −19° (*c* 4.83, $CHCl_3$); ir 1699 cm^{-1}; nmr δ 1.08 (s, 3), 0.88 (s, 3), 0.85 (s, 3), 0.84 (broad t, 3, *J* = 7 Hz).

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(23) L. I. Smith and K. L. Howard, *Org. Syn.*, **24**, 53 (1944).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.74; H, 10.73.

The methyl ester was prepared with diazomethane: $[\alpha]^{23}D$ +6° (*c* 6.46, $CHCl_3$); ir 1737 cm^{-1}; nmr δ 3.58 (s, 3), 0.97 (s, 3), 0.80 (s, 3), 0.78 (broad t, 3, J = 7 Hz), 0.77 (s, 3).

Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.80; H, 10.88.

Bromination–Dehydrobromination of Tricyclic Olefin 4.—A solution of 120 ml of acetic acid, 6.0 g of sodium acetate, and 6.2 ml (113.5 mmol) of bromine was added over a period of 20 min to a solution of 9.108 g (30.8 mmol) of 70% pure tricyclic olefin **4** in 125 ml of diethyl ether at 0°. The reaction mixture was allowed to react for 0.5 hr at 0° and poured into a solution of 10 g of sodium sulfite in water, and the product was extracted with hexane. The 15.42 g of crude dibromide was dissolved in 125 ml of γ-collidine and heated under reflux for 20 min under a N_2 atmosphere. The mixture was processed in the usual manner to yield 11.60 g of a brown oil which was chromatographed on 183 g of Woelm neutral alumina (activity II). Elution of the chromatography column with 570 ml of hexane produced 6.91 g of a fluid oil which was further purified by distillation through a 40 cm long platinum spinning band column (Nester–Faust) to yield 4.61 g of 63% pure tricyclic diene **32**, yield 46% by vpc analysis (20% DEGS, Chromosorb P, HMDS, 157°, 5 ft × 0.25 in.). A pure sample of tricyclic diene **32** was obtained by preparative glpc: bp 51° (3.0 mm); $[\alpha]^{23}D$ −73° (*c* 0.2897, $CHCl_3$); uv max (cyclohexane) 229 nm (ϵ 15,750), 236 (17,200), 245 (10,900); ir 3086, 3012, 1629, 1594, 889 cm^{-1}; nmr δ 6.05 (q, 1, J = 10, 2.5 Hz), 5.60 (broad d, 1, J = 10 Hz), 4.94 (narrow m, 1), 4.85 (broad s, 1), 1.10 (s, 3), 1.02 (s, 6).

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89.34; H, 10.72.

Treatment of Tricyclic Diene 32 with Potassium *tert*-Butoxide.—A mixture of 206 mg (0.82 mmol) of 80% pure tricyclic diene **32**, 4 ml of dry dimethyl sulfoxide, and 1.134 g (10.1 mmol) of commercial potassium *tert*-butoxide was allowed to react at 40° for 13 hr and then at 52° for 21 hr. The material was poured into aqueous sodium chloride and the product was isolated in the standard fashion. The 174 mg of a residual oil was chromatographed on 15.4 g of Woelm basic alumina (activity II); elution with 10 ml of hexane produced 47 mg of a colorless oil which had a superimpossible infrared spectrum with that of the 80% pure starting material. Further elution with 10 ml of hexane produced an additional 97 mg of impure diene **32** (infrared analysis). The tricyclic diene was purified by preparative vpc (20% DEGS, Chromosorb P, HMDS, 157°, 5 ft × 0.25 in.): $[\alpha]^{23}D$ −28° (*c* 0.2642, $CHCl_3$); uv max (cyclohexane) 229 nm (ϵ 15,700), 236 (16,600), 245 (10,000).

***p*-(*tert*-Amyl)toluene (33).**—A mixture of 63.7 ml of toluene and 67 ml of concentrated sulfuric acid was stirred under a nitrogen atmosphere at 0° while 16.4 ml (0.15 mol) of *tert*-amyl alcohol was slowly added over a period of 20 min such that the temperature of the mixture did not rise above 10°. The mixture was stirred at 0° for 2 hr, poured onto 1000 g of crushed ice, and the mixture was worked up to yield 24.2 g of a liquid which was distilled through a 40 cm long platinum spinning band column (Nester–Faust). The desired product, 13.98 g (57%), distilled at 93–99° (19 mm). The majority of the material distilled at 99° (19 mm) [lit[13] 100° (20 mm)]: nmr δ 6.83–7.29 (m, 4), 2.27 (s, 3), 1.62 (q, 2, J = 7 Hz), 1.23 (s, 6), 0.67 (t, 3, J = 7 Hz).

1-Methyl-4-*tert*-amylcyclohexa-1,4-diene (34).—A solution of 900 ml of liquid ammonia (distilled from sodium metal), 400 ml of diethyl ether, 370 ml of isopropyl alcohol, and 13.98 g (86.1 mmol) of *p*-(*tert*-amyl)toluene was stirred under reflux. A total of 12.9 g (1.86 mol) of lithium metal was added in portions to the reaction mixture over a period of 35 min. After stirring the reaction for an additional 10 min, the dark blue solution became colorless. The mixture was allowed to reflux for 1 additional hr and then 100 ml of methyl alcohol was added over a period of 10 min. Work-up in the standard fashion yielded 13.32 g (97%) of a colorless oil which by nmr spectral analysis was pure and contained no starting material. A portion of the material was further purified by preparative glpc (20% Carbowax 20M, 10% KOH, firebrick, 115°, 5 ft × 0.25 in.): ir 3015 cm^{-1}; nmr δ 5.41 (broad m, 2), 2.56 (broad s, 4), 1.65 (broad s, 3), 1.35 (broad q, 2, J = 7 Hz), 1.00 (s, 6), 0.71 (broad t, 3, J = 7 Hz).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.86; H, 12.09.

1-Methyl-4-*t*-amylcyclohexa-1,3-diene (35).—A mixture of 770 ml of dimethyl sulfoxide, 15 ml of benzene, and 13.32 g (81.2 mmol) of 1-methyl-4-*tert*-amylcyclohexa-1,4-diene (**34**) was stirred at room temperature for 0.5 hr while a nitrogen stream was bubbled through the solution. After addition of 25.2 g (225 mmol) of commercial potassium *tert*-butoxide, the reaction mixture was stirred for 27.75 hr, and worked up in the usual manner to yield 22.71 g of material which contained some hexane. Nmr analysis of the crude product indicated that the ratio of conjugated diene to unconjugated diene is 86:14. The material was distilled through a 40 cm long platinum spinning band column (Nester–Faust), bp 81–86° (10.5 mm), to yield 9.18 g (69%) of 90% pure product: bp 86° (10.5 mm); uv max (cyclohexane) 268 nm (ϵ 7285); nmr δ 5.53 (s, 2), 2.02 (s, 4), 1.75 (s, 3), 1.37 (broad q, 2, J = 7 Hz), 0.99 (s, 6), 0.72 (broad triplet, 3, J = 7 Hz).

The product rapidly reacted with air under ambient conditions to produce a viscous oil; a sample of the product obtained from the center fraction of the distillation gave the following analyses on successive days.

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 86.46; H, 12.66. *Anal.* Found: C, 79.85; H, 11.02.

1-Methyl-4-*tert*-amylbicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic Acid Anhydride (36).—A mixture of 9.00 g (54.8 mmol) of 90% pure 1-methyl-4-*tert*-amylcyclohexa-1,3-diene (**35**) (10% unconjugated diene), 35 ml of *o*-xylene (filtered through Woelm neutral alumina, activity I), and 5.50 g (56.1 mmol) of maleic anhydride, mp 53–54°, was heated for 2.7 hr at 135° under 1 atm of nitrogen. The yellow reaction mixture was worked up to yield 12.93 g (100%) of a white solid, mp 66–69°. This material was dissolved in benzene and filtered to remove insoluble material (*ca.* 50 mg), and the solvent was removed under reduced pressure. The residue had mp 72.5–74.0°; ir 3033, 1845, 1783, 708 cm^{-1}; nmr (benzene) δ 5.02 (d, 1, J = 8 Hz), 5.67 (d, 1, J = 8 Hz), 2.60 (d, 1, J = 9 Hz), 2.22 (d, 1, J = 9 Hz), 1.39 (s, 3), 0.98 (s, 3), 0.90 (s, 3), 0.82 (broad t, 3, J = 7 Hz).

Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 72.99; H, 8.30.

1-Methyl-4-*tert*-amylbicyclo[2.2.2]octane-2,3-dicarboxylic Acid (37).—A mixture of 12.12 g (46.2 mmol) of 1-methyl-4-*tert*-amylbicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic acid anhydride (**36**) and 98 mg of prereduced platinum oxide in 60 ml of tetrahydrofuran (distilled from lithium aluminum hydride) was shaken at room temperature under 1 atm of hydrogen gas. The absorption of hydrogen ceased after 6 hr. The mixture was processed to yield 11.46 g (94%) of a viscous oil which solidified overnight, mp 42–50°. A portion of the product was dissolved in hexane, the solution was filtered, and the solvent was removed under reduced pressure from the filtrate. The anhydride had mp 44–47°; ir 1862, 1776 cm^{-1}; nmr δ 3.17 (d, 1, J = 10 Hz), 2.83 (d, 1, J = 10 Hz), 1.13 (s, 3), 0.86 (s, 6), 0.85 (broad t, 3, J = 7 Hz).

Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.49; H, 9.10.

A mixture of 4.96 g (18.7 mmol) of the crude anhydride and 25 ml of 20% aqueous potassium bicarbonate was stirred on a steam bath for 1 hr, acidified, and extracted with ether. The solvent was rotary evaporated to yield 5.34 g of a light yellow foam. Approximately 70 ml of hexane was added to the foam, and the foam was scratched with a glass stirring rod to produce a white solid and a yellow solution. This mixture was filtered to yield 4.81 g (91%) of diacid **37**: mp 144.5–145.5° dec; ir (KBr) 1717 cm^{-1}; nmr ($CDCl_3$) δ 3.24 (d, 1, J = 11.5 Hz), 2.73 (d, 1, J = 11.5 Hz), 0.96 (s, 3), 0.80 (s, 6), 0.78 (broad t, 3, J = 7 Hz).

Anal. Calcd for $C_{16}H_{26}O_4$: C, 86.05; H, 9.28. Found: C, 67.99; H, 8.99.

1-Methyl-4-*tert*-amylbicyclo[2.2.2]octene (38).—A mixture of 10.10 g (38.2 mmol) of *cis*-1-methyl-4-*tert*-amylbicyclo[2.2.2]-octane-2,3-dicarboxylic acid (**37**), 70 ml of reagent grade benzene (filtered through Woelm neutral alumina, activity I), 4.93 ml of pyridine (distilled from *p*-toluenesulfonyl chloride and then potassium hydroxide), and 20.20 g (45.6 mmol) of lead tetraacetate (the material was washed free of acetic acid with dry hexane and the hexane was removed under reduced pressure to yield a white, free-flowing powder) was stirred for 50 min at room temperature under 1 atm of nitrogen. The orange opaque mixture was slowly heated in an oil bath until carbon dioxide began to evolve at 56°. At the end of 1.75 hr, the evolution of carbon dioxide had ceased. At this time, the mixture was heated at 75–80° for 3 hr and allowed to cool to room temperature and stand for an additional 3.75 hr. The mixture was poured into *ca.* 2 l. of 1.1 *M* aqueous nitric acid and extracted with diethyl ether until the aqueous layer was clear and colorless. The combined ethereal solutions were processed to yield 7.76 g of a fluid orange oil. Hexane was added and the mixture was filtered to yield a light yellow solution of the crude product in hexane. The solvent was evaporated under reduced pressure and the residual oil was chromatographed on 180 g of Woelm neutral alumina (activity I). Elution with 160 ml of hexane and evaporation of the solvent under reduced pressure yielded 4.80 g (65%) of the product as a colorless, mobile oil: ir 3021, 697 cm^{-1}; nmr δ 6.13 (d, 1, J = 8 Hz), 5.88 (d, 1, J = 8 Hz), 1.09 (s, 3), 0.85 (s, 6), 0.85 (broad t, 3, J = 7 Hz).

Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.37; H, 12.30.

1-Methyl-4-*tert*-amylbicyclo[2.2.2]octan-2-ol (40). A—A 30-ml aliquot of a solution of borane in tetrahydrofuran (1.26 *M* in boron hydride) was added to a stirred solution of 4.80 g (24.9 mmol) of 1-methyl-4-*tert*-amylbicyclo[2.2.2]octene (**38**) in 27 ml of tetrahydrofuran at 0°. After 15 min an additional 30 ml of borane solution was added and the mixture was allowed to warm to room temperature and react for 5.25 hr. The excess diborane was decomposed by the addition of 9 ml of water followed by the addition of 14.4 ml of 3 *M* aqueous sodium hydroxide and 14.4 ml of 30% aqueous hydrogen peroxide (no exothermic reaction). The mixture was stirred for 10 hr at room temperature, diluted with water, and extracted with four portions of diethyl ether. The combined ethereal solutions were worked up in the normal manner to yield 5.250 g of a viscous oil: ir 3635 (weak), 1360 cm^{-1} (strong); nmr δ 3.5–4.2 (multiplet). Vapor phase chromatographic analysis (20% Carbowax 20M, 10% KOH, Chromosorb W, 170°, 5 ft × 0.25 in.) showed three peaks in the ratio 24:64:12. The first peak had the same retention time as the starting bicyclic olefin. The second and third compounds eluted at a much longer retention time. The minor of the latter two compounds had a retention time 1.33 times longer than the major compound. Both of these latter compounds were collected by preparative glpc.

The minor product was a viscous oil, ir 3611 cm^{-1}, and the fingerprint region of the infrared spectrum was similar to that of the major product which was a white solid: mp 46–49°; ir 3611 cm^{-1}; nmr δ 3.97 (q, 1, J = 8.5, 2.5 Hz), 0.80 (broad s, 9), 0.79 (broad triplet, 3, J = 7 Hz). A dilute nmr spectrum of the minor product in carbon tetrachloride showed major absorptions for quaternary methyl groups at δ 0.80 and 0.70.

The remaining portion of the 5.250 g was chromatographed on 150 g of Woelm neutral alumina (activity II). Elution with 435 ml of hexane gave 1.29 g of a slightly viscous oil which had the same glpc retention time as bicyclic olefin **38**. Further elution of the chromatography column with 240 ml of diethyl ether yielded 2.07 g of a light yellow, viscous oil, glpc analysis of which showed that over 95% of the chromatogram consisted of the two previously mentioned alcohols in the ratio 4.4:1.0. The minor alcohol had the longer retention time. This mixture of alcohols was collected by preparative glpc.

Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 79.68; H, 12.22.

Further elution of the chromatography column with 100 ml of diethyl ether produced only 0.01 g of a viscous oil which was not investigated. The contents of the chromatography column were added to water, the mixture was extracted with three portions of diethyl ether, and the ethereal solution was processed in the usual manner to yield 0.53 g of a viscous boronic acid **45**: ir 3670, 3610, 3552, 3448, 1365 cm^{-1} (strong, broad); nmr δ 5.50 (very weak broad absorption), 1.0–2.0 (multiplet), 0.75 (strong singlet). An nmr spectrum of this material which was run less than 24 hr later showed no absorptions at δ 5.50. The strong singlet at δ 0.75 had been replaced by two strong overlapping broad singlets at δ 0.77 and 0.70 and the infrared spectrum no longer exhibited any oxygen–hydrogen stretching vibrations; these spectral features are characteristic of a boroxine **46**.

A solution of 460 mg of this latter material **46** in 10 ml of dry tetrahydrofuran was allowed to react with 1.0 ml of 30% aqueous hydrogen peroxide and 1.0 ml of 3 *M* aqueous sodium hydroxide under reflux for 2.3 hr. The mixture was diluted with water and extracted with three portions of diethyl ether. The combined ethereal solution was processed to yield 410 mg of a yellow oil. Analysis of the crude product by nmr and infrared spectroscopy showed major absorptions attributable to the major alcohol **40** in addition to a medium–strong absorption at 1365 cm^{-1} and a weak absorption at 3645 cm^{-1}. Glpc analysis showed only one compound, which was collected by preparative vpc. An infrared spectrum of this product was superimposible with a spectrum of the major alcohol **40**.

The remaining portion of the crude alcoholic product was dissolved in 10 ml of reagent grade acetone and treated with 0.5 ml of Jones reagent at 0°. The mixture was stirred and allowed to come to room temperature over a period of 15 min. The mixture was poured into water and the aqueous mixture was worked up in the usual manner to yield 372 mg of a light yellow oil. The nmr spectrum showed major absorptions attributable to ketone **42**.

B.—A solution of 5.63 g of 90% pure bicyclic olefin **38** (26.4 mmol) in 10 ml of dry tetrahydrofuran was allowed to react with 41.6 ml of 1.26 *M* boron hydride in tetrahydrofuran at room temperature for 45.5 hr. The borane adduct was oxidized by the addition of 4.74 ml of 3 *M* aqueous sodium hydroxide and 4.74 ml of aqueous 30% hydrogen peroxide and heating the mixture at 47° for 1 hr. The solution was processed in the standard manner to yield 6.54 g of a viscous yellow oil. The material was chromatographed on 150 g of Woelm neutral alumina (activity II). Elution with 300 ml of hexane gave 1.63 g of an oil with no nmr absorptions downfield from δ 2.0; only the complex absorptions of hydrogens substituted on nonfunctionalized carbon atoms were seen between δ 0.6 and 2.0. Further elution with 340 ml of diethyl ether gave 4.11 g of a viscous oil; glpc analysis of the material showed the presence of two alcohols **40** and **39** in the ratio 2.6:1.0 at the same retention times as the two alcohols mentioned in the first experiment; the minor alcohol had the longer retention time.

1-Methyl-4-*tert*-amylbicyclo[2.2.2]octan-2-one 42.—A solution of 848 mg (4.0 mmol) of the mixture of bicyclic alcohols **40** and **39**, containing some boroxine from the hydroboration experiment, in 25 ml of acetone at 0° was oxidized with 1.0 ml (1.0 equiv) of Jones reagent to yield 821 mg (98%) of a fluid, light yellow oil. Glpc analysis of the material (10% KOH, 20% Carbowax 6000, firebrick, 172°, 5 ft × 0.25 in.) indicated that two ketones were formed in the ratio of 2.0:1.0 (by area); the minor ketone had the longer retention time.

The minor ketone **41** was purified by preparative glpc (same conditions as above): ir 1722 cm^{-1}; nmr δ 2.07 (broad s, 2), 0.87 (s, 3), 0.85 (broad t, 3, J = 7 Hz), 0.78 (s, 6).

The major ketone **42** was purified by preparative glpc: ir 1718 cm^{-1}; nmr δ 1.95 (broad s, 2), 0.92 (s, 3), 0.88 (s, 6), 0.81 (broad t, 3, J = 7 Hz).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.42; H, 11.31.

1-Methyl-4-*tert*-amylbicyclo[2.2.2]octane-2,3-dione (43a).—A mixture of 1.521 g (7.33 mmol) of the 2.0:1.0 mixture of bicyclic ketones **42** and **41**, 11.5 g (104 mmol) of selenium dioxide, and 20 ml of *o*-xylene was stirred for 10 hr in an oil bath at 140–145°. The mixture was processed in the standard fashion and a hexane concentrate was analyzed by glpc (G.E. SF-96, 170°, 5 ft × 0.25 in.; chromatography on 10% KOH, 20% Carbowax 20M, Chromosorb W, 172°, 5 ft × 0.25 in. decomposed the product to a carbonyl-containing compound, ir 1718 cm^{-1}). The hexane solution was evaporated under reduced pressure to yield a brown residual oil which chromatographed on 50 g of silica gel (the product was unstable on Woelm neutral alumina, activity II). The column was eluted with 600 ml of benzene and the solvent was evaporated under reduced pressure to yield 1.508 g of an amber oil which solidified. The material was recrystallized from pentane to yield a total of 697 mg (43%) of product: mp 90–91°; uv max (cyclohexane) 456 nm (ε 33); ir 1750, 1732 cm^{-1}; nmr δ 1.00 (s, 3), 0.94 (s, 6), 0.86 (broad t, 3, J = 7 Hz).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98. Found: C, 75.48; H, 9.72.

1-Methyl-4-*tert*-amylbicyclo[2.2.2]octane-2,3-dione 2-*p*-Toluenesulfonylhydrazone (43b).—A mixture of 636 mg (2.86 mmol) of 1-methyl-4-*tert*-amylbicyclo[2.2.2]octane-2,3-dione (**43a**), 533 mg (2.86 mmol) of *p*-toluenesulfonylhydrazine, and 7.5 ml of chloroform was stirred for 48 hr with the exclusion of light. The mixture was filtered through anhydrous sodium sulfate and the solvent was removed under reduced pressure to yield 981 mg (88%) of bicyclic keto hydrazone **43b**. A portion of the product was recrystallized from chloroform–methyl alcohol to yield small, light yellow needles: mp 193° (decomposition with gas evolution); uv max (EtOH) 229 nm (ε 9710), 289 (10,400), 397 (242); ir 3218, 1680, 1371, 1166 cm^{-1}; nmr δ 7.83 (broad d, 2, J = 8 Hz), 7.30 (broad d, 2, J = 8 Hz), 2.43 (s, 3) 1.05 (s, 3), 0.92 (s, 6), 0.83 (broad triplet, 3, J = 7 Hz).

Anal. Calcd for $C_{21}H_{30}N_2SO_3$: C, 64.58; H, 7.74; N, 7.17; S, 8.21. Found: C, 64.31; H, 8.03; N, 7.33; S, 8.10.

2-Diazo-1-methyl-4-*tert*-amylbicyclo[2.2.2]octan-3-one (43c).—A solution of 764 mg (1.96 mmol) of 1-methyl-4-*tert*-amylbicyclo[2.2.2]octane-2,3-dione 2-*p*-toluenesulfonylhydrazone (**43b**) in 10 ml of chloroform was filtered through 21 g of Woelm basic alumina (activity I). The column was eluted with fresh chloroform until appreciable amounts of a yellow eluate were no longer obtained. The chloroform solution was concentrated under reduced pressure. An infrared spectrum of the concentrated solution indicated that some unreacted hydrazone was present in the mixture. The mixture was filtered again through 21 g of Woelm basic alumina (activity I). Fresh chloroform was passed through the column until the yellow diazo ketone no longer eluted from the column. The solvent was removed under reduced pressure to yield 343 mg (75%) of diazo ketone **43c**, mp 66–69°. A small portion of the product was recrystallized from hexane at −78° to yield a pure sample of the product as light yellow needles: mp 69–70°; uv max (cyclohexane) 265 nm (ϵ 12,700), 424 (15); ir 2078, 1651 cm^{-1}; nmr δ 1.22 (s, 3), 0.98 (s, 6), 0.85 (broad t, 3, J = 7 Hz).

Anal. Calcd for $C_{14}H_{22}ON_2$: N, 11.96. Found: N, 12.08.

Irradiation of Diazo Ketone 43c in Water.—Nitrogen gas was slowly bubbled through a solution of 118 mg (0.50 mmol) of 2-diazo-1-methyl-4-*tert*-amylbicyclo[2.2.2]octan-2-one (**43c**) in 25 ml of 70% aqueous tetrahydrofuran (seven parts tetrahydrofuran which had been distilled from lithium aluminum hydride, three parts water, by volume) for 30 min. The solution was irradiated in a quartz irradiation flask with a 679A-36 Hanovia 450-W quartz mercury vapor lamp and a Corex 9700 filter (transmission: 0%, 255 mμ; 50%, 290 mμ) for 20 min under 1 atm of helium gas. After standing for 1 hr at room temperature, the solution was diluted with 75 ml of 1 *M* aqueous potassium hydroxide and extracted with two volumes of diethyl ether. The combined ethereal solutions were washed with water and saturated aqueous sodium chloride and dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure to yield 91 mg (95%) of crude 1-methyl-4-*tert*-amylbicyclo[2.2.1]-heptyl-7-ketene (**44**): uv max (cyclohexane) 222 nm (ϵ 1260), 301 (shoulder), 386 (15); ir 2115 cm^{-1}; nmr δ 1.33 (s, 3), 0.93 (s, 6), 0.88 (broad t, 3, J = 7 Hz).

A portion of this crude product, 44 mg, was heated under reflux for 30 min in a solution of 1.5 ml of ethylene glycol dimethyl ether (distilled from lithium aluminum hydride), 0.5 ml of water, and 180 μl of 70% aqueous perchloric acid. After this time an additional 1.5 ml of ethylene glycol dimethyl ether and 0.5 ml of water were added and the solution was heated under reflux for an additional 30 min. The solution was allowed to stand for 12 hr at 0°, diluted with 30 ml of 1 *M* aqueous potassium hydroxide, and extracted with diethyl ether. The alkaline extracts yielded 35 mg (70% based on diazo ketone **43c**) of a colorless oil which solidified. An infrared spectrum of the crude product in carbon tetrachloride was identical with the spectrum of bicyclic acid **25a** obtained from the degradation of tricyclic olefin **4**. A portion of the material was recrystallized from pentane, mp 80.5–81.5°, pK^*_{MCS} 8.44.[21]

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.12; H, 10.55.

A portion of the acidic product was esterified in the usual manner with diazomethane in diethyl ether to yield 78 mg of product. The infrared and nmr spectra of this esterified material were identical in all respects with the spectra of methyl ester **25b** which was obtained from the irradiation of diazo ketone **43c** in anhydrous methyl alcohol. A portion of this ester, 60 mg, did not hydrolyze in a solution of 9 ml of methyl alcohol, 1 ml of water, and 1.21 g of potassium hydroxide pellets, which was heated under reflux for 6.5 hr.

Treatment of Tricyclic Ketone 14 with Trifluoroperacetic Acid.—A methylene chloride solution of 39.6 mmol of trifluoroperacetic acid was added to a mixture of 1.14 g (5.2 mmol) of tricyclic ketone **14**, 12.8 g (90 mmol) of sodium hydrogen phosphate, and 100 ml of methylene chloride. The reaction mixture was stirred and heated under reflux for 8.25 hr. The reaction mixture was worked up in the standard fashion to yield 1.14 g of a light yellow oil which slowly crystallized to yield 280 mg of a white solid, mp 138–140°. The filtrate was concentrated and placed in the refrigerator for 2 days. Filtration gave an additional 102 mg of crude product, mp 100–123°. The total yield of tricyclic lactone **47** was 382 mg (31%). Chromatography of the mother liquors from the recrystallizations on Woelm neutral alumina (activity II) gave an 11% yield of unreacted ketone and a small yield (4%) of an isomeric lactone, ir 1736 cm^{-1}. In addition a complex mixture of unknown alcohols and ketones were eluted from the chromatography column with hexane–diethyl ether. These products were not investigated.

Tricyclic lactone **47** could not be purified by alumina chromatography because it would not elute from the column with diethyl ether. When the chromatography column was stripped with water, a mixture of lactone **47** and its corresponding hydroxy acid were isolated. A portion of the crude tricyclic lactone was recrystallized two times from hexane: mp 142–143°; $[\alpha]^{23}\mathrm{D}$ −40° (c 1.11, $CHCl_3$); ir 1729 cm^{-1}; nmr δ 4.67 (q, 1, J = 7 Hz), 1.27 (d, 3, J = 7 Hz), 1.00 (s, 3), 0.88 (s, 3), 0.73 (s, 3).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.39; H, 10.05.

Treatment of Tricyclic Lactone 47 with Boron Trifluoride in Methyl Alcohol.—A mixture of 234 mg (0.99 mmol) of tricyclic lactone **47**, 30 ml of dry methyl alcohol, and 1.7 ml of boron trifluoride etherate (freshly distilled) was heated under reflux in 1 atm of nitrogen for 23.5 hr. The solution was cooled to room temperature and allowed to react for an additional 20.5 hr. The solution was worked up in the standard fashion to yield 238 mg of a light yellow, semisolid material which was chromatographed on 10 g of Woelm neutral alumina (activity II). Elution with 104 ml of hexane yielded 124 mg (50%) of bicyclic unsaturated ester **48**: $[\alpha]^{23}\mathrm{D}$ −2° (c 10.74, $CHCl_3$); ir 3086, 1745, 1639, 898 cm^{-1}; nmr δ 4.93 (s, 1, $W_{1/2}$ = 2.0 Hz), 4.79 (m, 1, $W_{1/2}$ = 2.3 Hz), 3.59 (s, 3), 2.35 (septet, 1, J = 7 Hz), 1.08 (s, 3), 0.97 (s, 6).

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.76; H, 10.47. Found: C, 77.03; H, 10.64.

Preparation of Bicyclic α-Bromo Esters (49).—A mixture of 263 mg (1.11 mmol) of bicyclic acid **22a**, 5 ml of purified thionyl chloride, and 220 mg (1.37 mmol) of bromine was heated under reflux for 10.5 hr. The mixture was cooled and dropped slowly into methyl alcohol at 0°. The methanolic solution was stirred for 12 hr at room temperature, and processed in the usual way to yield 363 mg (99%) of the crude product. The product was a mixture of two diastereoisomers: $[\alpha]^{23}\mathrm{D}$ +15° (c 1.575, $CHCl_3$); ir 1755, 1728 cm^{-1}; nmr δ 4.80, 4.77, 4.66, 4.58 (the four absorptions integrated to a total of one hydrogen), 3.73, 3.71 (the two absorptions integrated to a total of three hydrogens).

Calcd relative intensities for $C_{14}H_{22}O_2Br^+$: m/e 301, 1.000; 303, 0.9923. Found: m/e 301, 1.000; 303, 1.00 ± 0.05.

Dehydrohalogenation of α-Bromo Esters 49.—A solution of 347 mg (1.05 mmol) of α-bromo esters **49** in 6 ml of synthetic quinoline was heated at 172° for 2 hr. The mixture was allowed to cool to room temperature and was poured into 0.65 *M* aqueous hydrochloric acid. The mixture was worked up in the usual manner and the residual 186 mg of brownish-red oil was chromatographed on 18 g of Woelm neutral alumina (activity II). Elution with 72 ml of hexane yielded 45 mg of an multicomponent oil and further elution with 80 ml of hexane gave 44 mg (17%) of hydrocarbon **50**: $[\alpha]^{23}\mathrm{D}$ 0° (c 2.71, $CHCl_3$); uv max (cyclohexane) 194 nm (ϵ 14,700), 204 (13,800); ir max 3021, 1725, 1653 cm^{-1}; nmr δ 6.85 (d, 1, J = 16 Hz), 5.63 (d, 1, J = 16 Hz), 5.37 (m, 1), 3.27 (s, 3), 1.80–2.15 (m, 4), 1.05 (s, 3), 0.97 (s, 6), 0.67 (t, 3, J = 7 Hz); mass spectrum m/e 250.

Further elution with hexane–diethyl ether yielded an additional 62 mg of material but no fraction contained spectral absorptions characteristic of the desired unrearranged product.

Registry No.—**1**, 32435-95-3; **4**, 32391-40-5; **12**, 32434-51-8; **13**, 32434-52-9; **13** 2,4-DNP, 32434-53-0; **14**, 32434-54-1; **14** 2,4-DNP, 32460-86-9; **15**, 32434-55-2; **16**, 32434-56-3; **17**, 32434-57-4; **18**, 32434-58-5; **19**, 32434-59-6; **20**, 32434-60-9; **21a**, 32460-87-0; **21b**, 32434-61-0; **22a**, 32434-62-1; **22b**, 32434-63-2; **23**, 32434-64-3; **24**, 32434-65-4; **25a**, 32434-84-7; **25a** methyl ester, 32434-85-8; **27b**, 32434-66-5; **32**, 32460-88-1; **33**, 4237-70-1; **34**, 32434-68-7; **35**, 32434-69-8; **36**, 32434-70-1; **37** anhydride, 32434-71-2; **37**, 32434-72-3; **38**, 32434-83-6; **40**, 32434-73-4; **41**, 32434-74-5; **42**, 32434-75-6; **43a**, 32434-76-7; **43b**, 32434-77-8; **43c**, 32434-78-9; **44**, 32460-89-2; **45**, 32434-79-0; **47**, 32460-90-5; **48**, 32434-80-3; **49**, 32434-81-4; **50**, 32434-82-5.