20%; 180 min, *ca.* 5%. Analysis of a similar reaction mixture containing 0.12 g (0.0075 mole) of α,o,o,p-tetramethylstyrene in the same manner showed the following amounts of 1-decene remaining at the indicated times: 30 min, 70%; 60 min, 50%; 120 min, 10%.

Registry No.—*p*-Methylstyrene, 622-97-9; o,p-dimethylstyrene, 2234-20-0; styrene, 100-42-5; α,p-dimethylstyrene, 1195-32-0; α-methylstyrene, 98-83-9; o,o,p-trimethylstyrene, 769-25-5; α,o,p-trimethylstyrene, 14679-12-0; α,o,o,p-tetramethylstyrene, 14679-13-1; bromotrichloromethane, 75-62-7; 1-butanethiol, 109-79-5; 3-bromo-3-(*p*-methylphenyl)-1,11-trichloropropane, 14679-14-2; 3-bromo-3-(o,p-dimethylphenyl)-1,1,1-trichloropropane, 14679-15-3; 2-phenylethyl *n*-butyl sulfide, 14679-16-4; 2-phenylpropyl *n*-butyl sulfide, 14679-17-5; 2-(*p*-methylphenyl)ethyl *n*-butyl sulfide, 14723-35-4; 2-(o,p-dimethylphenyl)ethyl *n*-butyl sulfide, 14679-18-6; 2-(o,o,p-trimethylphenyl)ethyl *n*-butyl sulfide, 14746-02-2; 2-(*p*-methylphenyl)propyl *n*-butyl sulfide, 14679-19-7; 2-(o,p-dimethylphenyl)propyl *n*-butyl sulfide, 14679-20-0.

Highly Strained Bicyclic Systems. XII. Synthesis and Solvolysis of 1,5,5-Trimethylbicyclo[2.1.1]hex-2-yl *p*-Toluenesulfonate[1-3]

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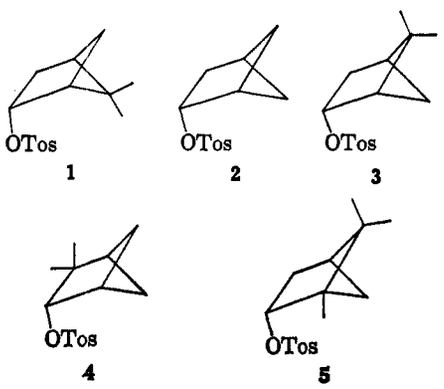
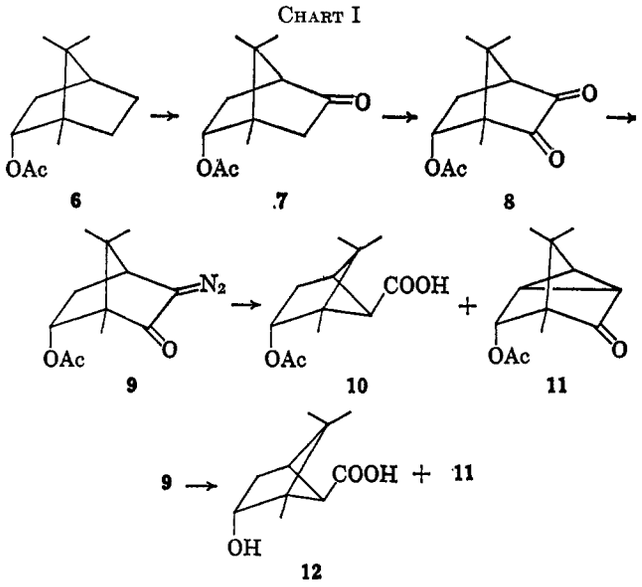
The synthesis of 1,5,5-trimethylbicyclo[2.1.1]hex-2α-yl *p*-toluenesulfonate (**5**) from *l*-bornyl acetate (**6**) is described. Acetolysis of **5** results chiefly in the formation of a ring-opened product, **25a**. The solvolysis rate shows that significant enhancement results from the presence of the bridgehead methyl group at C_1, in accord with positive charge delocalization to this position in the transition state.

Earlier in this series an argument has been presented favoring the view that the acetolysis of a 2-substituted bicyclo[2.2.1]hexane (**1**) showed marked rate enhancement compared with a hypothetical, classical model.[5] Recently, the parent ester, bicyclo[2.1.1]hex-2-yl *p*-toluenesulfonate (**2**), was prepared and studied in this laboratory.[6,7] Data on the effect of methyl substituents on the rate of solvolysis of this tosylate were also obtained *via* the synthesis and solvolysis of tosylates **3**[6,7] and **4**.[6,7] It was of interest in this connection to synthesize tosylate **5** in order to study the effect of the introduction of a bridgehead methyl group at C_1 on the solvolysis rate as compared with the rates of those esters already studied.



Synthesis of 1,5,5-Trimethylbicyclo[2.1.1]hex-2-yl *p*-Toluenesulfonate.—In order to make use of the valuable Horner and Spietschka[8] bicyclo[2.1.1]hexane synthesis, the acetoxy diazo ketone **9** was required. This compound was prepared and utilized as shown in Chart I.

CHART I



The direct chromic acid oxidation of bornyl acetate (**6**) to 5-ketobornyl acetate (**7**) has been described by Bredt and Goeb.[9] In our hands this oxidation gave modest yields of crystalline **7**, mp 78°. The diketone **8**, mp 103–105°, was prepared by selenium dioxide oxidation of **7** in acetic anhydride, as described by Asahina and coworkers.[10]

Asahina, *et al.*,[11] have prepared the diazo ketone **9** by oxidation of the monohydrazone of ketone **8** with mercuric oxide. This method was found to be less satisfactory than the base decomposition of the *p*-toluene-

(1) The partial support of this research by grants (G-22,541 and GP-4128) from the National Science Foundation, and by Hoffmann-LaRoche, Inc., is acknowledged with pleasure.

(2) For the previous paper in this series, see J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966).

(3) Taken in part from the Ph.D. dissertation submitted by J. C. Shelton to Cornell University, Ithaca, N. Y., Sept 1964.

(4) Department of Chemistry, The University, Glasgow, Scotland.

(5) J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **85**, 57 (1963).

(6) Abstracts, 18th National Organic Chemistry Symposium, Columbus, Ohio, June 16–20, 1963, pp 37–44.

(7) See also ref 2.

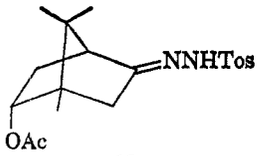
(8) L. Horner and E. Spietschka, *Ber.*, **88**, 934 (1955).

(9) J. Bredt and A. Goeb, *J. Prakt. Chem.*, **101**, 273 (1921).

(10) Y. Asahina, M. Ishidate, and T. Tukamoto, *Ber.*, **69**, 349 (1936).

(11) Y. Asahina, M. Ishidate, and T. Tukamoto, *ibid.*, **69**, 355 (1936).

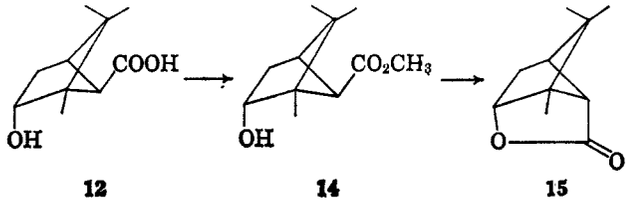
sulfonylhydrazone of **8**. This intermediate was not isolated, but was converted directly into the desired diazo ketone **9**.[12] The diazo ketone was obtained as a bright orange-yellow crystalline solid, mp 116.5° (lit.[11] mp 120°). A white solid, mp 138–139°, could be eluted from the alumina column with methanol after elution of the diazo ketone was complete. The infrared spectrum and analysis of this solid were in accord with its formulation as 5-ketobornyl acetate *p*-toluenesulfonylhydrazone (**13**), derived from the small amount of residual **7** in the diketone used.



13

The irradiation of **9** was carried out in aqueous dioxane using a Hanovia 500-w mercury lamp in a quartz immersion well. After a few hours of irradiation, the white, crystalline acetoxy acid **10**, mp 108–110°, was obtained in 50–70% yield. Another product was a pale yellow, neutral oil (*ca.* 20%), shown to be the tricyclic keto acetate **11** on the basis of evidence to be discussed below. The photochemical ring contraction of **9** could also be carried out using Sylvania "Blacklites" as the ultraviolet source over a period of 7–10 days. Under these conditions the acetate group was hydrolyzed, giving the hydroxy acid **12**, mp 180–181°. This same hydroxy acid could be prepared by hydrolysis of **10** with aqueous sodium hydroxide at room temperature.

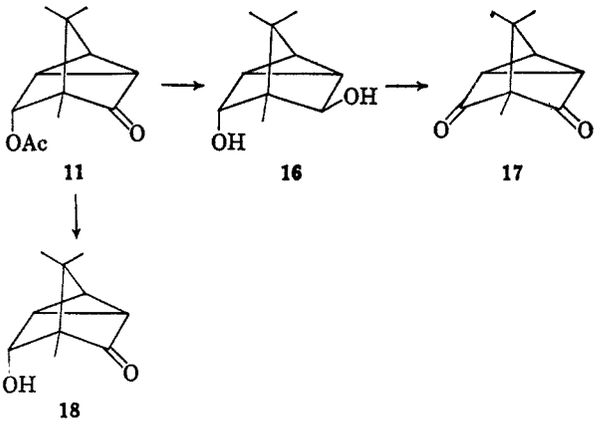
The *exo* configuration of the carboxyl group in **12** was demonstrated by the fact that this compound failed to lactonize upon vacuum distillation or upon acidification of an aqueous solution. In contrast, lactonization could be readily effected following epimerization of the corresponding methyl ester **14**. Thus, treatment of **12** with ethereal diazomethane gave the crystalline methyl ester **14**, mp 54°. This ester was hydrolyzed with concomitant epimerization[13] using potassium hydroxide in aqueous ethanol. Acidification of the basic solution gave the lactone **15**, mp 127–129°. Its infrared spectrum (carbon tetrachloride) showed a split carbonyl peak at 5.57 and 5.63 μ, very similar to that observed for other lactones of this type.[2]



12 **14** **15**

It should be noted that it is uncertain, on the basis of the method of synthesis, whether the diazo group of **9** was at C_5 or C_6. Although this ambiguity in the structure of **9** is not important for the synthesis of **12**, it was possible to assign this intermediate structure unambiguously. Simple steric considerations would require that the C_5 carbonyl group would react preferentially, but the possibility of the acetoxy group on C_2 exerting a directive influence by complexing with the reagent in some way could not be ruled out. Since the diazo ketone had a sharp melting point, it seems reasonable to assume that it is one isomer. Proof that the neutral oil, formed as a side product in the photolysis of **9**, has structure **11** removes this structural ambiguity, since the isomeric diazo ketone could hardly be expected to give a tricyclic product of this type. The structure of **11** was demonstrated in two ways as outlined in Chart II.

CHART II



11 **16** **17**

18

The acetoxy ketone **11**, $[\alpha]^{25}D$ 85 ± 3° (absolute ethanol), was reduced with lithium aluminum hydride to give the diol **16** as a white, crystalline solid, mp 246–247°, $[\alpha]^{25}D$ 109 ± 5° (absolute ethanol). Assuming for the moment that the structures are correct, the stereochemistry of this diol would be expected to be as shown on the basis of other studies of the lithium aluminum hydride reduction of related molecules,[14,15] and it is confirmed by the optical activity of this diol. Oxidation of **16** with chromic acid in pyridine gave the dione **17**, mp 203–204°, which was found to be optically inactive, as required for this structure. The nmr spectrum of **17** showed sharp methyl group singlets at τ 9.00 and 9.37 (6 H and 3 H, respectively), and a complex multiplet centered at 7.4 (3 H) corresponding to the three remaining cyclopropyl protons. The infrared spectrum of **17** showed a pair of carbonyl peaks at 5.55 and 5.71 μ, not unlike that of an acid anhydride, to which it bears a formal similarity. Confirmatory evidence was obtained by hydrolysis of **11** under mild conditions (sodium carbonate in aqueous methanol) to give the known keto alcohol **18**, mp 233–234° (lit[11] mp 234°), $[\alpha]^{25}D$ 28 ± 10° (absolute ethanol).

Continuing with the major synthetic objective, it was necessary to decarboxylate the acetoxy acid **10** and to hydrolyze the resulting acetate **21** to give the alcohol **22** from which the tosylate **5** could be made for solvolysis studies. The decarboxylation method of Wiberg[16] was employed as outlined in Chart III.

The acid chloride **19** was prepared by treating **10** with oxalyl chloride in dry benzene and was converted directly into the *t*-butyl per ester **20** by treatment with *t*-butylhydroperoxide and pyridine. The per ester was pyrolyzed in *p*-cymene at 150° to give **21**, which was

(12) *Cf.* J. M. Muchowski, *Tetrahedron Letters*, 1773 (1966).

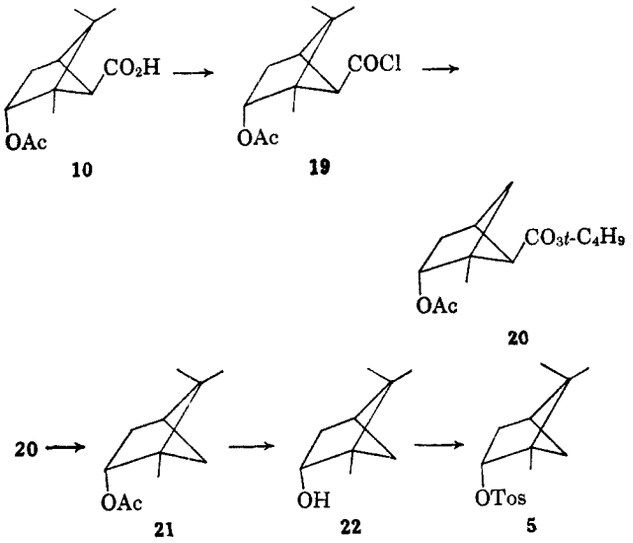
(13) J. Meinwald, A. Lewis, and P. G. Gassman, *J. Am. Chem. Soc.*, **84**, 977 (1962).

(14) W. G. Brown, *Org. Reactions*, **6**, 475 (1961).

(15) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 304.

(16) K. B. Wiberg, B. Lowry, and T. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).

CHART III



reduced to **22** with lithium aluminum hydride. Chromatography on alumina followed by preparative glpc gave the very volatile, colorless, crystalline alcohol **22** in *ca.* 15% over-all yield from **10**. This alcohol could be further purified by sublimation to give **22** as colorless crystals, mp 105°. Acetylation of **22** by the standard pyridine–acetic anhydride procedure gave **21**.

The tosylate **5**, prepared by the usual method, was obtained as a colorless, crystalline solid, mp 55°. This ester was very unstable and would decompose to a black tar if permitted to stand at room temperature overnight. Therefore, acetolysis studies had to be carried out immediately using the freshly prepared tosylate.

Solvolysis Results.—The acetolysis of **5** was carried out in the usual manner.[6,17,18] When the acetolysis was carried out at 75°, the reaction was essentially over before the first sample could be titrated, indicating that the half-life was much less than 4 min. Consequently, the acetolyses were carried out at 25 and 50°, and the rate constant at 75° was calculated from these data. The experimental and calculated data are summarized in Table I.

TABLE I

Temp, °C	k, sec^{-1}	$t_{1/2}$, sec
25.01 + 0.02	2.81×10^{-5}	2450
49.97 ± 0.02	6.73×10^{-4}	1020
75.00[a]	1.05×10^{-2}	66.3

[a] Calculated.

As stated earlier, one purpose of this study was to determine the effect of an alkyl substituent at C_1 on the rate of solvolysis of **5** as compared with esters **1–4**. The relevant data are summarized in Table II. A discussion of the effects of the alkyl groups in these tosylates has already been presented in terms of charge delocalization in the transition state for solvolysis.[19] Because of the electron-releasing ability of an added methyl group at C_1, it was predicted that the rate of

(17) S. Winstein, E. Grunwald, and C. Hanson, *J. Am. Chem. Soc.*, **70**, 812 (1948).

(18) S. Winstein, E. Grunwald, and L. Ingraham, *ibid.*, **70**, 821 (1948).

(19) J. Meinwald and Y. C. Meinwald in "Advances in Alicyclic Chemistry," H. Hart and G. Karabatsos, Ed., Vol. 1, Academic Press Inc., New York, N. Y., 1966. See also ref 7, as well as J. K. Crandall, Ph.D. dissertation, Cornell University, Ithaca, N. Y., Sept 1963.

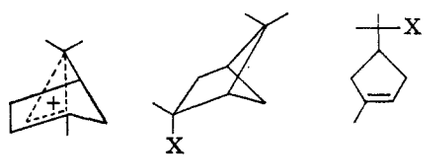
TABLE II

Compd	$k \times 10^5$, sec^{-1}	Temp, °C	Rel rate
1	56.1 ± 1.4	75.10 ± 0.02	30
2	1.89 ± 0.01	74.70 ± 0.02	1.0
3	67.8 (65.1)[a]	74.67 ± 0.02	35
4	1.55 ± 0.01	75.10 ± 0.02	0.8
5	1050[b]	75.00	560

[a] Run on impure tosylate. [b] Calculated from rate constants at 25 and 50°.

acetolysis of a C_1 methylated substrate would increase. In fact, Table II shows that tosylate **5** solvolyzes at a rate more than 15 times that of tosylate **3**, and at a rate of 560 times that of tosylate **2**. This accelerative effect of the methyl group is, therefore, in accord with expectations based on a bridged structure such as **23** or a rearranged, tertiary structure for the resultant ion. One may wonder alternatively whether the C_1 methyl might have a similar effect as a result of the introduction of a new, nonbonded repulsion with the departing group. Consideration of scale molecules, however, does not make this alternate rationalization attractive, since there should be almost perfect staggering (about 60° dihedral angle) between the departing C_2 tosylate group and the bridgehead methyl group.

Considering that the ion formed from tosylate **5** may be the bridged ion **23** or the closely related, rearranged tertiary ions, one would expect the possible acetolysis products to be **21**, **24a**, and **25a**, which upon reductive cleavage would give the corresponding alcohols **22**, **24b**, and **25b**. Glpc analysis of the acetolysis products



23 **24a**, X = OAc; **b**, X = OH **25a**, X = OAc; **b**, X = OH

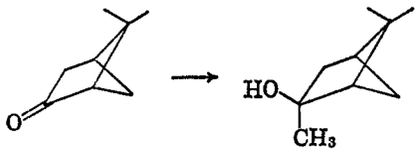
showed that the crude acetate mixture contained 98% of one compound and 2% of another. The 2% component had a retention time identical with that of **21**, showing that the major product must be rearranged. The infrared spectrum of the crude acetate mixture confirmed this conclusion.

Reductive cleavage of the acetate mixture to the corresponding alcohols with lithium aluminum hydride gave a mixture which was analyzed by glpc. It showed two peaks: A, 92%, and B, 8%. The nature of B is unclear, since it showed an unexpectedly long retention time, and all alcohol isomers of A studied had retention times very close to that of A, and it is possible that it was an artifact. A was shown not to be chromatographically identical with **22**, supporting the data from the acetate mixture.

An attempt was made to synthesize alcohol **24b** by treatment of the known ketone **26**[20] with methyl lithium, hoping that the great reactivity of the reagent would make it indiscriminate enough to give both possible epimeric alcohols. However, a colorless, crystalline alcohol, mp 70.5°, was obtained, which appeared to be chromatographically pure **27** (glpc analysis), even before any purification attempt was made. Attempts to

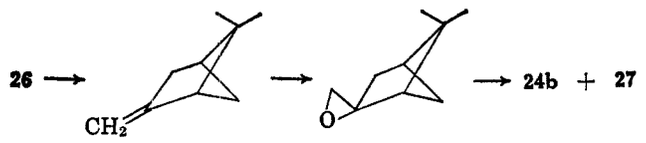
(20) J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 2857 (1960); **82**, 5445 (1960).

prepare the alcohol **24b** by addition of methyl magnesium iodide to the ketone **26** also failed, again giving pure **27**.



26 **27**

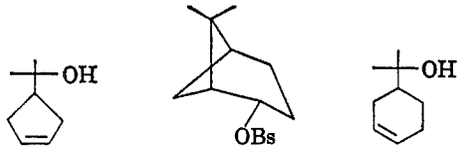
Alcohol **24b** was finally synthesized using a different approach. Treatment of the ketone **26** with Wittig reagent gave olefin **28**. Attempts to carry out this reaction in ether under the usual conditions gave mainly recovered starting material. However, the method of Corey,[21] employing dimethylsulfoxide as solvent and the corresponding anion as base, was successful. The olefin was oxidized to the epoxide **29**, whose stereochemistry is assigned on the basis of the steric hindrance to be expected for topside attack, by treatment with *m*-chlorobenzoic acid. This epoxide seemed to contain a small amount of its stereoisomer, since it was reduced with lithium aluminum hydride to give a mixture of **24b** (93%) and the previously characterized **27** (7%). With an authentic sample of **24b** in hand, a direct comparison with the major solvolysis product was possible, and it was found that the two were not identical.



28 **29**

By this process of elimination, the only logical remaining structure for the chief solvolysis reduction product was that shown in formula **25b**. Preparation of an authentic sample of this compound was accomplished easily by the treatment of the ethyl ester of 1-methylcyclopentene-4-carboxylic acid[22] with methyl magnesium iodide. A direct comparison of the nmr spectra of **25b** from solvolysis and from this synthesis showed them to be identical.

That the ring-opened alcohol **25b** would be the primary product in the solvolysis of **5** is not unexpected, since the ring-opened alcohol **30** is a major product (35%) in the solvolysis of **1**, and it is the main product (98%) in the solvolysis of the analogous tosylate **3**.[7,19] In a recent study of the acetolysis of β-nopinyl *p*-bromobenzene sulfonate (**31**), Winstein[23] has shown the ring-opened alcohol **32** to be one of the major products.



30 **31** **32**

Experimental Section

All boiling points and melting points are uncorrected. Anhydrous magnesium sulfate was used as drying agent unless otherwise stated. Nmr spectra were taken in carbon tetrachloride with tetramethylsilane as an internal standard, using a Varian A-60 spectrometer. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Schwarzkopf Microchemical Laboratory, Woodside 77, N. Y. All glpc analyses were carried out on an Aerograph Model 600 Hy-Fl. Preparative glpc chromatography was done on a Beckman GC-2 gas chromatograph.

***endo*-2-Acetoxy-1,7,7-trimethylbicyclo[2.2.1]heptan-5-one (7) (5-Ketobornyl Acetate).**[9,10]—A mixture of 50.0 g (0.256 mole) of 1-bornyl acetate (Aldrich Chemical Company, Milwaukee, Wis.) and 75 ml of glacial acetic acid in a 2-l., three-necked flask fitted with a reflux condenser was stirred and heated at 140° on an oil bath. A slurry was prepared from 125 g (1.25 moles) of chromic oxide and 175 ml of glacial acetic acid. This slurry was added through the top of the reflux condenser as smoothly as possible over a period of 55 min, washing down the condenser between additions with a small amount of glacial acetic acid (total volume 150 ml). The slurry was added in such a way as to keep the reaction mixture in a state of constant frothing. Heating and stirring were continued for 30 min after addition and the mixture was allowed to cool to room temperature. The crude reaction mixture was diluted with 1.5 l. of water and extracted several times with ether (total volume 1.5 l.). The ether solution of 5-keto bornyl acetate was washed with 100-ml portions of 5% sodium hydroxide, with saturated sodium bicarbonate solution until the solution was definitely basic, and then with water. The ether solution was dried and the ether was removed on the flash evaporator. The resulting oil was vacuum distilled; the first distillation fractions consisted of bornyl acetate and camphor. The 5-ketobornyl acetate, which was collected at 78–80° (0.1 mm), consisted of 22.5 g of a mixture of crystals and oil. The oil was removed by washing with a small amount of pentane, and the solid was recrystallized from hexane to give 12.2 g (23%) of white crystals (mp 66–69°). Futher recrystallization gave pure 5-ketobornyl acetate (mp 78°, lit.[10] mp 78°). The yield varied in this reaction without apparent reason over the range 15–35%. Optimum yields were obtained only on relatively small-scale reactions using less than 100 g of bornyl acetate.

***endo*-6-Acetoxy-1,7,7-trimethylbicyclo[2.2.1]heptan-2,3-dione (8) (*endo*-6-Acetoxycamphorquinone).**[10]—A mixture of 10.0 g (0.0476 mole) of 5-ketobornyl acetate and 13.0 g (0.117 mole) of *freshly sublimed* and *pulverized* selenium dioxide in 10 ml of acetic anhydride was stirred in a 100-ml, three-necked, round-bottom flask fitted with a reflux condenser. The mixture was heated and stirred on an oil bath at 135° for 16 hr. The reaction mixture was cooled to room temperature and diluted with ether to precipitate selenium. The selenium was filtered off and the ether and acetic anhydride were removed on the flash evaporator. The remaining dark oil was dissolved in 200 ml of ether and washed with 50-ml portions of water and saturated sodium bicarbonate solution. (*N.B.* If most of the acetic anhydride was not removed, emulsions resulted at this point.) The ether solution was finally washed several times with water, dried, and concentrated on the flash evaporator to remove solvent. The residue was a dark red-brown solid (7.38 g) which was sublimed at 100° (0.3 mm) to give 6.50 g of bright yellow crystals. Recrystallization from aqueous methanol gave 6.32 g (59%) of yellow diketone melting at 103–105° (lit.[10] mp 109°), $[\alpha]^{25}D$ −190° (*c* 0.373, absolute ethanol) (lit.[10] $[\alpha]^{25}D$ − 191.4°). This diketone was still contaminated with a small amount of starting monoketone, but its further purification was unnecessary.

3-Diazo-*endo*-6-acetoxy-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (9).[24]—To 30.0 g (0.134 mole) of diketone **8** in 150 ml of chloroform was added 26.1 g (0.140 mole) of *p*-toluenesulfonylhydrazine in one lot. The resulting suspension was stirred at room temperature for 23 hr. The monotosylhydrazone was not isolated from the reaction mixture, but was converted directly into the desired diazo ketone as described below.

The solution was filtered to remove a small amount of white solid, and was then poured directly onto 1 kg of alumina (Fisher Scientific Co., adsorption alumina, 80–200 mesh, Cat. No. A-540) in a large, wide column (8.5-cm diameter) and eluted with chloroform. The bright yellow solution of diazo ketone which was eluted in this way was stripped of solvent on the flash evaporator, yielding 25.7 g (81%) of a bright orange-yellow,

(21) E. J. Corey, R. Greenwald, and M. Chaykovsky, *J. Org. Chem.*, **28**, 1128 (1963).

(22) P. D. Bartlett and G. D. Sargent, *J. Am. Chem. Soc.*, **87**, 1297 (1965).

(23) S. Winstein and E. Friedrich, *ibid.*, **86**, 2721 (1964).

(24) J. Meinwald, *Record Chem. Prog.* (Kresge-Hooker Sci. Lib.), **22**, 39 (1961).

crystalline solid. This solid was recrystallized from hexane to give 22.4 g (71%) of diazo ketone, mp 116.5° (lit.[11] mp 120°).

Elution of the column with methanol and removal of the solvent on the flash evaporator gave a yellow oil which crystallized when washed with hexane–ether mixture. Filtration gave 2.8 g of a white solid which was recrystallized from methanol–ether (1:4) to give a white solid, mp 138–138.5°. The infrared spectrum (Nujol) of this white solid was nearly identical with that of authentic 5-ketobornyl acetate tosylhydrazone. (See below.)

Anal. Calcd for $C_{19}H_{26}O_4SN_2$: C, 60.29; H, 6.92; S, 8.47; N, 7.40. Found: C, 59.67; H, 6.78; S, 8.39; N, 7.46.

2α-Acetoxy-1,5,5-trimethylbicyclo[2.1.1]hexane-*exo*-6-carboxylic Acid (10).—A solution of 18.5 g (0.0784 mole) of diazoketone **9** in 500 ml of Spectrograde *p*-dioxane and 400 ml of distilled water was deoxygenated with a slow stream of nitrogen for 20 min and irradiated for 3.5 hr in a quartz vessel using an unfiltered 500-w Hanovia mercury lamp. A very slow stream of nitrogen was bubbled through the solution during the photolysis. A 1-ml sample was withdrawn and worked up at the end of this time. The infrared spectrum of the product showed no remaining diazo peak at 4.85 μ, and the entire yellow solution was concentrated on the flash evaporator to remove 75% of the solvent. The aqueous solution was then made alkaline with aqueous sodium carbonate solution and extracted with ether several times to remove neutral products. The ether solution of the neutral product was washed with water several times, dried, and concentrated on the flash evaporator to give 3.35 g of an orange oil. Distillation of this material gave *endo*-2-acetoxy-1,7,7-trimethyltricyclo[2.2.1.$0^{3,5}$]heptan-6-one (**11**) as a pale yellow oil, bp 103° (1.8 mm), $[\alpha]^{25}D$ −85 ± 3° (*a* = 0.33, *c* 0.389, absolute ethanol). The infrared spectrum (neat film) showed absorptions at 3.42 (m), 5.70 (s), 5.77 (s), 6.92 (w), 7.38 (m), 7.51 (w), 7.71 (w), 8.06 (s), 8.62 (w), 9.09 (vw), 9.60 (m, broad), 9.95 (w), 10.57 (w), 10.88 (w), 11.10 (w), 11.34 (w), 11.78 (w), 12.21 (w) μ. (See below.)

The aqueous solution was carefully acidified with cold dilute sulfuric acid to pH 3–5. The pale yellow solid which precipitated was filtered off and dissolved in ether. The ether solution was dried and evaporated on the flash evaporator to give 9.71 g of a pale yellow solid. The acidified aqueous solution was extracted with ether and the ether solution washed with water. After drying, removal of the ether gave 2.92 g of a yellow solid slightly wet with an oil. The total yield of crude acid was 12.6 g (71%). Recrystallization from aqueous methanol gave 6.62 g of a colorless crystalline solid, mp 108–110°, which sublimed at 105° (20 mm).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.69; H, 8.02. Found: C, 63.99; H, 8.29.

The mother liquors were concentrated under vacuum to give an oily acetoxy acid which crystallized upon standing. This acid could be conveniently used without further purification for the preparation of 1,5,5-trimethylbicyclo[2.1.1]hexan-2α-ol (**22**).

1,5,5-Trimethylbicyclo[2.1.1]hexan-2α-ol-*exo*-6-carboxylic Acid (12).—Attempted hydrolysis of the acetoxy acid **10** with aqueous sodium carbonate at room temperature gave only starting material.

A solution of 0.60 g (2.7 mmoles) of acetoxy acid **10** in 6.0 ml of 1.0 *M* sodium hydroxide (6.0 mmoles) and 12 ml of water was stirred at room temperature for 9 hr. The solution was cooled on an ice bath and carefully acidified with cold dilute sulfuric acid, giving a colorless solid which was filtered and washed with water several times. This solid was dried under vacuum for 3 hr, and then at room temperature overnight to give 0.42 g (86%) of a colorless product, mp 180–181°. This material could be recrystallized from aqueous methanol and sublimed at 130° (0.05 mm). This same hydroxy acid was prepared by slow photolysis of an aqueous dioxane solution of diazo ketone in Pyrex test tubes with Sylvania "Blacklite" ultraviolet lamps.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.22; H, 8.70. Found: C, 65.39; H, 9.00.

1,6,6-Trimethylbicyclo[2.1.1]hexan-2α-ol-5-*exo*-carboxylic Acid Methyl Ester (14).—A solution of 2.80 g (0.0152 mole) of the hydroxy acid **12** in 15 ml of methanol was cooled in an ice bath, and excess ethereal diazomethane was added until the solution was definitely yellow in color. The resulting solution was kept at room temperature for 3 hr and then filtered to remove a small amount of solid. The solvent was removed to give a yellow oil which crystallized to give 2.62 g (87%) of a pale yellow solid. Recrystallization from pentane gave colorless crystals, mp 53.5–54.5°. The infrared spectrum (Nujol) showed absorptions at 3.05 (m), 3.45 (vs), 5.80 (s), 6.86 (s), 7.27 (m), 8.12 (m), 8.39 (w), 8.85 (m), 9.49 (m), 9.70 (w), 9.96 (w), 10.94 (w), 12.86 (w) μ.

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.87; H, 9.09. Found: C, 66.81; H, 9.20.

1,6,6-Trimethylbicyclo[2.1.1]hexan-2α-ol-*endo*-5-carboxylic Acid Lactone (15).—A solution of 500 mg of hydroxy ester **14** in 4.0 ml of ethanol was refluxed with 0.5 g of potassium hydroxide in 1.3 ml of water for 1.5 hr. The alcohol was removed under vacuum and the aqueous solution was acidified with dilute hydrochloric acid. An initial precipitate formed which redissolved. Upon warming on a steam bath, the solution turned milky and a crystalline precipitate came out which was very soluble in hexane, but could be recrystallized from water. The product was sublimed at 80–100° (0.7 mm) to give colorless crystals which melted at 127–129° with previous softening and subliming. The infrared spectrum (carbon tetrachloride) showed absorptions at 3.38 (m), 5.57 (vs), 5.63 (vs), 6.89 (m), 7.19 (w), 7.28 (w), 7.48 (w), 7.59 (m), 7.80 (w), 8.30 (vw), 8.47 (m), 8.56 (s), 8.83 (w), 9.00 (vw), 9.10 (m), 9.29 (w), 9.88 (m), 10.24 (s), 10.68 (m), 10.90 (w), 11.12 (m), 11.57 (w), 14.29 (m) μ.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.28; H, 8.43. Found: C, 72.48; H, 8.55.

***endo*-2-Acetoxy-1,7,7-trimethylbicyclo[2.2.1]heptan-5-one *p*-Toluenesulfonylhydrazone (13).**—A solution of 1.05 g (0.005 mole) of 5-ketobornyl acetate and 0.93 g (0.0050 mole) of *p*-toluenesulfonylhydrazine in 7.0 ml of methanol was heated briefly at the boiling point on a steam bath and left at room temperature overnight. The solvent was removed on a steam bath, giving a thick gum which turned into a white crystalline solid upon the addition of ether. The solid was separated by filtration and recrystallized from ethyl acetate to give **13**, mp 152–153°. The infrared spectrum (Nujol) of this product was identical with that of the white solid isolated from the mother liquor in the preparation of the diazo ketone (**9**): 3.12 (w), 3.4–3.5 (vs, broad), 5.85 (m), 6.27 (w), 6.87 (s), 7.10 (m), 7.27 (m), 7.41 (m), 7.66 (w), 7.90 (m), 8.00 (m), 8.41 (w), 8.57 (m), 8.72 (w), 9.00 (w), 9.13 (w), 9.65 (w), 9.79 (w), 9.93 (m, broad), 10.48 (w), 10.93 (w), 11.58 (vw), 12.14 (m), 12.43 (vw, broad), 13.56 (vw, broad), 14.12 (vw) μ.

Anal. Calcd for $C_{19}H_{26}O_4SN_2$: C, 60.29; H, 6.92; N, 7.40; S, 8.47. Found: C, 60.19; H, 6.87; N, 7.95; S, 8.82.

1,7,7-Trimethyltricyclo[2.2.1.$0^{3,5}$]heptane-*endo*-2-*exo*-6-diol (16).—A solution of 4.0 g (0.019 mole) of tricyclic acetoxy ketone **11** in 75 ml of dry ether was added dropwise to a stirred suspension of 8.0 g (0.21 mole) of lithium aluminum hydride in 200 ml of dry ether at room temperature. The mixture was stirred for 1.5 hr after the addition was complete. The suspension was cooled in an ice bath and 40 ml of water was added dropwise with stirring. After stirring overnight, the ether solution was decanted from the inorganic solids and these solids were washed well with ether. The ether solution was dried and concentrated under vacuum to remove solvent, giving a quantitative yield of colorless, crystalline diol **16**. The diol was insoluble in most solvents, but very soluble in methanol. It was recrystallized from methanol–chloroform (1:50) and from methanol–ether (1:15) to give colorless crystals, mp 246–247° (with slight decomposition), $[\alpha]^{25}D$ −109 ± 5° (*a* = −0.21, *c* 0.193, absolute ethanol). The infrared spectrum (Nujol) showed absorptions at 3.02 (m), 3.42 (s), 6.88 (m), 7.28 (w), 7.81 (w), 8.30 (vw), 8.60 (vw), 8.92 (vw), 9.28 (m), 9.43 (m), 9.57 (s), 10.28 (vw), 11.00 (vw), 12.09 (w) μ.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.08; H, 9.60.

1,7,7-Trimethyltricyclo[2.2.1.$0^{3,5}$]heptane-2,6-dione (17).—Sarett reagent was prepared in the usual way: 16 ml of dry pyridine was cooled to 10–20° and 2.62 g (26.2 mmoles) of chromium trioxide was added slowly with stirring and occasional gentle cooling. To this stirred suspension of the complex in pyridine was added a solution of 440 mg (2.62 mmoles) of the diol **16**, $[\alpha]^{25}D$ −109 ± 5° (absolute ethanol), dissolved in 6.0 ml of dry pyridine. The reaction mixture was heated on a water bath at 45–55° with stirring for 40 min, after which stirring was continued at room temperature for 16 hr longer. The dark mixture was poured into 100 ml of water and extracted with ether several times (125 ml total volume). The ether solution was washed with water, dilute sulfuric acid, and water and was dried. The solvent was removed on the flash evaporator to give 350 g (81%) of a colorless solid which was recrystallized from hexane and sublimed at 70° (1.0 mm). Resublimation of this dione gave optically inactive (ethanol solvent) colorless crystals, mp 203–204°.

The infrared spectrum (carbon tetrachloride) showed absorptions at 3.46 (w), 5.55 (s), 5.71 (s), 6.58 (m), 7.51 (w), 8.00 (w-broad), 8.30 (w), 9.15 (w), 10.00 (w-broad), 10.21 (w), 10.69 (w) μ. The nmr spectrum showed sharp singlets for the methyl groups at τ 9.0 and 9.37 (6 H and 3 H, respectively) and a complex multiplet centered at 7.4 (1 H).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.28; H, 7.46.

1,7,7-Trimethyltricyclo[2.2.1.0^{2,6}]heptan-*endo*-2-ol-6-one (18).—A mixture of 1.00 g (4.81 mmoles) of keto acetate **11** and 0.510 g (4.81 mmoles) of sodium carbonate in 15 ml of distilled water and 10 ml of methanol was heated briefly on a steam bath to bring about solution, and was then allowed to stand at room temperature overnight. The resultant mixture was extracted with ether and the ether solution was washed with water to remove methanol. After drying, the ether was removed to give 200 mg (25%) of a pale yellow solid. Extraction of the aqueous solution with chloroform gave a small additional amount of product. Recrystallization of this product from hexane gave 140 mg of colorless solid, mp 220–250°. Recrystallization from hexene–ether gave crystals, mp 232–235°. After two sublimations at reduced pressure the solid melted at 233–234° (lit.[11] mp 234°), $[\alpha]^{25}D$ 28 ± 10° (a = 0.02, c 0.072, absolute ethanol). The infrared spectrum (carbon tetrachloride) showed signals at 2.74 (w), 2.89 (w), 3.37 (m), 5.67 (s), 6.83 (w), 6.90 (w), 7.18 (s), 7.73 (w), 9.40 (m), 96.2 (w), 10.11 (w), 10.39 (w), 10.85 (w), 11.33 (w), 11.86 (w) μ.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.48. Found: C, 72.26; H, 8.59.

1,5,5-Trimethylbicyclo[2.1.1]hexan-2α-ol (22).—To a stirred solution of 3.50 g (0.0155 mole) of acetoxy acid **10** in 50 ml of dry benzene at room temperature was added 6.0 ml (9.0 g; 0.071 mole) of oxalyl chloride. The flask was fitted with a drying tube and the reaction mixture was stirred overnight. The benzene was removed on the flash evaporator to give 3.80 g of the acid chloride **19** as a crude oil. The infrared spectrum (neat) showed absorptions at 3.48 (m), 5.55 (s), 5.60 (s), 5.76 (vs), 6.88 (w), 7.27 (m), 7.99 (vs), 8.10 (vs), 8.39 (w), 8.5–8.6 (vw-broad), 8.70 (vw), 8.90 (vw), 9.21 (m), 9.41 (s), 9.61 (s), 10.47 (w), 10.64 (vw), 11.4 (vw, broad), 11.7–11.8 (vw, broad), 12.11 (w), 13.44 (m, broad), 14.05 (vw) μ.

The acid chloride was dissolved in 15 ml of *p*-cymene and added dropwise to a stirred solution of 1.67 g (0.0186 mole) of *t*-butyl hydroperoxide and 2.0 ml of dry pyridine in 15 ml of *p*-cymene on an ice bath. Stirring was continued for 3.5 hr after the addition was complete. The reaction mixture was then poured onto 60 g of ice and stirred. The organic layer was separated and the aqueous layer was extracted with a few milliliters of *p*-cymene. The combined organic solutions were washed with ice water, cold 5% sulfuric acid, ice water, cold saturated sodium bicarbonate, and ice water and were dried.

The flask containing the dried *p*-cymene solution of the per ester **20** was fitted with a reflux condenser, several boiling chips were added, and the solution was pyrolyzed on an oil bath at 150 ± 5° for 80 min. (The vigorous reaction marked by evolution of gas was over in about an hour.) The resulting solution of acetate **21** was cooled and diluted with 50 ml of dry ether.

The ethereal *p*-cymene solution of the acetate was added dropwise to a stirred suspension of 5.1 g (0.14 mole) of lithium aluminum hydride in 100 ml of dry ether at room temperature. The resulting mixture was stirred for 3.5 hr and then placed on an ice bath. Stirring was continued as 20 ml of water was added slowly. After stirring overnight the inorganic salts were filtered and washed well with ether. The ether solution was dried and the ether removed carefully by slow distillation through a 20-in. Vigreux column. The remaining *p*-cymene solution was chromatographed on 100 g of alumina. Elution with pentane removed the *p*-cymene. Elution with ether brought off the alcohol fraction. The solvent was carefully distilled from the alcohol through a 20-in. Vigreux column until the residual volume was about 2 ml. The alcohol **22** was isolated by preparative glpc on a 10% Carbowax (4) column at 160° to give a colorles solid, mp 96–100°. This material was sublimed at atmospheri pressure at 80–85°, yielding **22** (320 mg, 15%), mp 104.5–105°. The infrared spectrum (Nujol) gave 2.99 (m), 3.46 (vs), 6.87 (vw), 7.28 (s), 7.80 (w), 7.97 (w), 8.16 (vw), 8.25 (w), 8.39 (vw), 8.48 (w), 8.70 (w), 9.02 (m), 9.58 (m), 10.00 (w), 10.20 (vw), 10.46 (vw), 10.65 (vw), 10.81 (w), 11.19 (w), 11.82 (m), 13.80 (w, broad) μ.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.40. Found: C, 76.96; H, 11.40.

The acetate of this alcohol **22** was prepared by allowing a solution of 43 mg of alcohol **22**, 4 drops of acetic anhydride, and four drops of dry pyridine to stand at room temperature for 24 hr. Cold water was dropped in slowly to hydrolyze excess acetic anhydride, and the solution was extracted with ether. The ether solution was washed with cold solutions of dilute sulfuric acid, water, saturated sodium bicarbonate, and water. Drying, followed by removal of the ether on the flash evaporator gave 36 mg of an oil which gave a single glpc peak on a 5% Silicone column at 98° (retention time 7 min). The infrared spectrum (neat film) showed absorptions at 3.38 (s), 5.77 (vs), 6.71 (w), 6.81 (m), 6.90 (m), 7.27 (s), 7.77 (m), 7.96 (vs), 8.04 (vs), 8.39 (w), 8.68 (vw), 9.01 (m), 9.49 (m), 9.64 (s), 10.42 (w), 11.02 (vw), 11.66 (vw), 11.90 (w) μ.

1,5,5-Trimethylbicyclo[2.1.1]hex-2α-yl *p*-Toluenesulfonate (5).—Solid *p*-toluenesulfonyl chloride (832 mg, 4.36 mmoles) was added in small portions with swirling to a cooled solution of 565 mg (4.36 mmoles) of alcohol **22** in 2.0 ml of dry pyridine on an ice bath. After solution was achieved, the mixture was left to stand in the refrigerator for 41 hr. A few drops of cold water were added and the solution was allowed to stand for 20 min to hydrolyze the excess *p*-toluenesulfonyl chloride. The mixture was then poured onto several grams of ice and extracted with ether. The ether solution was washed with 8–10-ml portions of cold water, cold dilute sulfuric acid, cold water, cold saturated sodium bicarbonate, and cold water. The ether solution was then dried and the solvent removed on the flash evaporator at room temperature to give 1.08 g (93%) of a crude solid. This solid was recrystallized from cold hexane to give 877 mg (76%) of a colorless solid which decomposed to a black tar if permitted to stand at room temperature overnight. The crude mother liquor could be kept for 2 weeks in the refrigerator before decomposing.

The tosylate freshly prepared by this procedure showed mp 55°. The infrared spectrum (Nujol) showed absorptions at 3.4–3.5 (vs, broad), 6.25 (m), 6.83–6.90 (s, broad), 7.28 (s), 7.41 (s), 7.67 (vw), 7.75 (w), 8.23 (w), 8.39 (s), 8.47 (s), 9.10 (m), 9.46 (vw), 9.88 (w), 10.12 (m), 10.29 (m), 10.54 (m), 10.79 (m), 11.29 (s, broad), 11.79 (m), 12.09 (m), 12.71 (w), 14.04 (m) μ. Analysis was not possible because of the instability of this tosylate.

Acetolysis of 1,5,5-Trimethylbicyclo[2.1.1]hex-2α-yl *p*-Toluenesulfonate (5).—Acetolyses were carried out in dry acetic acid in the usual manner.[6,17,18] Titrations of aliquots were performed using bromphenol blue as indicator. In a preliminary run, a solution which was 0.0500 M each in tosylate and fused sodium acetate was solvolyzed in sealed ampoules in an oil bath 74.98 ± 0.02°. Titrations were made with 0.0208 M perchloric acid in acetic acid. At this temperature the reaction was complete before the first titration was made (4 min).

Acetolyses were then carried out in a volumetric flask immersed in constant temperature baths at 25.01 ± 0.02° and at 49.97 ± 0.02°. Samples were withdrawn at appropriate intervals and titrated. The rate constants at these temperatures were calculated, and the rate constant at 75.00° was calculated from this data.

Preparative Acetolysis of 5.—A solution of 939 mg (3.19 mmoles) of **5** and 313 mg (3.82 mmoles) of fused sodium acetate in 4.0 ml of dry acetic acid was heated in an oil bath at 75.0° for 10.5 min (*ca.* 10 half-lives). The solution was cooled to room temperature and poured onto several grams of ice in 20 ml of water. After efficient stirring, the solution was extracted with ether. The ether was washed with water, cold saturated sodium carbonate solution, and water, and dried. Several milliliters of this solution were withdrawn for infrared spectral and glpc analyses. The remainder of the dried ether solution was reduced with lithium aluminum hydride directly. (See below.) The infrared spectrum (neat) showed absorptions at 3.43 (m), (shoulders at 3.29, 3.37, 3.52), 5.77 (s), 6.92 (w), 7.31 (s), 7.97 (s), 8.12 (w), 8.40 (vw), 8.49 (vw), 8.61 (vw), 8.85 (w), 9.80 (w), 10.23 (vw, broad), 11.36 (vw, broad), 12.57 (vw, broad) μ. Glpc analysis on a 5% silicone column at 96° gave two peaks: A, 2% (7.3 min), and B, 98% (8.2 min).

The main portion of the dried ethereal acetate solution was added slowly to a stirred suspension of 1.21 g (0.032 mole) of lithium aluminum hydride in 25 ml of dry ether at room temperature. Stirring was continued for 9 hr after addition was complete. The reaction mixture was cooled in an ice bath, and 6.0 ml of water was added slowly with stirring. Stirring was con-

tinued for 3 hr. The mixture was filtered to remove the inorganic salts and the salts were washed well with ether. The combined ether solution was dried and the solvent removed on the flash evaporator to give 369 mg of a pale yellow oil. Glpc studies on a 10% Carbowax column (20M) at 146° showed two peaks: A, 92% (9.7 min), and B, 8% (14.2 min). Mixed glpc analyses of this mixture with authentic samples of **22**, **24b**, and **27** on a 5% silicone column at 90–95° and also on a 10% Carbowax column (20M) at 138–168° showed them to be chromatographically identical with neither component of the mixture, although retention times for these isomers were very close to that of the main product. The pale yellow hydroxylic product was twice distilled at 65–75° (0.07 mm) to give 64 mg of a colorless oil. The infrared spectrum (neat) showed absorptions at 2.93 (m), 3.28 (shoulder), 3.37 (m), 3.42 (m), 5.81 (vw), 5.89 (vw), 6.02 (vw), 6.82 (w), 7.29 (m), 7.58 (vw), 7.84 (vw), 7.97 (vw), 8.49 (w), 8.75 (w, broad), 9.34 (vw), 9.82 (w), 10.67 (w), 11.6–11.7 (w, broad), 12.58 (m) μ. The nmr spectrum proved identical with that of authentic **25b**, described below.

2,5,5-Trimethylbicyclo[2.1.1]hexan-2β-ol (27).—To a stirred solution of 15.0 ml of dry ether and 1.5 ml (3.40 g; 0.016 mole) of methyl iodide in a 25-ml, round-bottomed flask fitted with a reflux condenser was added 400 mg (0.0577 g-atom) of lithium metal in small pieces. The mixture was stirred at room temperature for 7 hr under a nitrogen atmosphere. The resultant solution of methyl lithium was filtered through a small amount of glass wool into a dropping funnel and added slowly to a solution of 125 mg (1.01 mmoles) of 5,5-dimethylbicyclo[2.1.1]-hexan-2-one (**26**) in 15 ml of dry ether which was cooled in an ice bath and stirred. After stirring overnight, 2.0 ml of water was added slowly to the stirred solution and a white solid separated. The solution was filtered and washed several times with water. After drying, the solvent was carefully distilled off through a short Vigreux column. Removal of the last traces of solvent with a stream of nitrogen gave 121 mg (86%) of a colorless solid which gave a single gas chromatographic peak on a 5% silicone column at 89° (retention time 3.5 min) and on a 20% Carbowax column at 158° (retention time 13.3 min). The product was sublimed twice at atmospheric pressure and 60–65° to give **27** as colorless crystals, mp 70.5°. The infrared spectrum (Nujol) had a broad peak at 3.01 μ and no peaks in the carbonyl (5.5–6.0 μ) region. The nmr spectrum showed singlets at τ 8.87, 8.73, 8.64, and 7.35 (areas 3:3:3:1, respectively), characteristic of the methyl and hydroxyl groups.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.40. Found: C, 77.24; H, 11.54.

2,5,5-Trimethylbicyclo[2.1.1]hexan-2α-ol (24b).—A 54.7% suspension of sodium hydride in mineral oil (0.989 g, 0.0255 mole) was washed with pentane to remove the mineral oil and dried with a stream of dry nitrogen, leaving a grey solid. Dry dimethylsulfoxide[21] (15 ml) was added and the mixture heated on an oil bath at 70–85° with stirring for 0.5 hr until the evolution of hydrogen had ceased. The clear solution was cooled in an ice bath while stirring was continued. When a warm solution of 8.05 g (0.0225 mole) of triphenylmethylphosphonium bromide in 16 ml of dimethylsulfoxide was added, the solution turned dark orange. This solution was stirred for 15 min at 35°. The ketone **26** (2.00 g, 0.0161 mole) was added dropwise, and the solution was stirred and heated on an oil bath at 60° for 22 hr. The dimethylsulfoxide solution was poured into 70 ml of water and filtered through a sintered glass funnel to remove precipitated triphenylphosphine oxide. The solution was extracted with pentane. The organic solution was washed with water and saturated sodium chloride, and dried. The pentane solution was then poured through 50 g of alumina rather quickly to rid the pentane solution of triphenylphosphine oxide, dimethyl sulfoxide, and other polar compounds, and the column was eluted with another 50 ml of pentane. The pentane was removed by distillation through a 20-in. Vigreux column until the remaining volume was about 5 ml. This pentane solution gave a single glpc peak on a 20% Carbowax column at 85° (retention time 6 min). The infrared spectrum (pentane) showed absorptions at 5.99 (s), 7.88 (m), 8.07 (m), 9.32 (m), 9.60 (m), 10.17 (w), 10.52 (m), 11.48 (s), 12.22 (m) μ. The olefin solution was used without further purification for preparation of the epoxide **29**.

A solution of 3.00 g (85% minimum purity, 0.016 mole, minimum) of *m*-chloroperbenzoic acid in 10 ml of dry ether was stirred in an ice bath. The above olefin in pentane was added and stirring continued in the ice bath for 4 hr, during which time a white precipitate appeared. The mixture was stirred at room temperature for 43 hr longer and cooled in an ice bath before filtering to remove the precipitate. The solution was then washed with aqueous sodium carbonate solution, aqueous ferrous ammonium sulfate solution, aqueous sodium carbonate solution (several times after the wash water was basic), and water. The solution was dried and the ether was distilled off through a long column to give 1.11 g of an oil. The infrared spectrum (neat film) showed absorptions at 3.36 (s), 5.63 (w), 5.80 (m), 6.37 (vw), 6.71 (m), 6.87 (m), 7.14 (m), 7.22 (w), 7.31 (w), 7.77 (w), 7.93–8.00 (m, broad), 8.21 (w), 8.92 (m), 9.18 (m), 10.82 (m), 10.53 (m), 10.98 (m), 11.13 (m), 11.62 (w), 12.07 (w), 12.48 (m), 13.3 (m, broad) μ.

The crude epoxide above was dissolved in 20 ml dry ether and added dropwise to a stirred suspension of 1.0 g (0.027 mole) of lithium aluminum hydride in 40 ml of dry ether. The mixture was stirred for 3.5 hr at room temperature and refluxed for 3.5 hr longer. The stirred mixture was then cooled in an ice bath and 6.0 ml of water was added dropwise. Stirring was continued for 3 hr at room temperature after addition was complete. The inorganic salts were then filtered off and washed well with ether, and the combined ether solutions were dried. The ether was removed by careful distillation through a long column to give 760 mg of an oil. Glpc analysis on a 10% Carbowax column at 142° gave two peaks: A (8.5 min, 7%) and B (9.8 min, 93%). A was shown to be **27** by a mixed chromatograph with an authentic sample. An attempt to isolate the main alcohol **24b** by preparative glpc on a 10% Carbowax column at 144° resulted in improvement of purity to 97%, but at a great loss of product. The infrared spectrum (neat) showed absorptions at 2.95 (m), 3.39 (s), 6.86 (m), 7.26 (m), 7.73 (m), 7.93 (w), 8.10 (w), 8.37 (m), 8.95 (s), 9.48 (vw), 9.81 (w,broad), 10.68 (m), 11.14 (m), 12.20 (w) μ.

Synthesis of 25b.—Ethyl 2-isopropenylcyclopropane-1-carboxylate was prepared and pyrolyzed as described by Bartlett and Sargent.[22] In our hands, the pyrolysis, carried out at 498–500°, gave a 29% yield of the expected 1-methylcyclopentene-4-carboxylic acid, accompanied by a 36% yield of the corresponding ethyl ester, bp 69–71° (5.5 mm); its nmr spectrum was comparable with that of the free acid, with additional ethyl absorption (τ 5.92, quartet; 8.88, triplet).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.93; H, 9.34.

Methylmagnesium iodide was prepared from 17.5 g of methyl iodide, 3 g of magnesium, and 200 ml of absolute ether in the usual way. The Grignard reagent was cooled and 7.8 g of ethyl 1-methylcyclopentene-4-carboxylate in 50 ml of absolute ether was added dropwise, with stirring, over a 1-hr period. The resultant mixture was kept at reflux for 1 hr, cooled, and poured into a mixture of 200 g of ice and 400 ml of 20% aqueous ammonium chloride solution. The ether layer was separated, and the aqueous layer washed twice with water. The combined ether extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated to leave crude **25b**. Distillation of the residue at 63° (4 mm) gave 6 g (86%) of the **25b** as a colorless liquid.

In the infrared spectrum, this product showed absorption at 2.87, 3.39, 6.90, 7.25, 8.84, 10.70 and 12.55 μ. The nmr spectrum (CCl_4 solution) showed absorptions at τ 4.85 (1 H), 7.25 (1 H), 7.77 (5 H), 8.32 (3 H), and 8.95 (6 H). The 7.25 peak disappeared after exchange with D_2O. These spectra compared well with those obtained previously from **25b** obtained from the solvolysis of **5**.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.05; H, 11.29.

Registry No.—**1**, 15188-53-1; **2**, 15188-52-0; **3**, 15188-53-1; **4**, 15188-54-2; **5**, 15188-55-3; **7**, 10293-01-3; **8**, 15188-57-5; **9**, 15188-58-6; **10**, 15188-59-7; **11**, 15350-58-0; **12**, 15188-60-0; **13**, 15188-61-1; **14**, 15259-07-1; **15**, 15188-51-9; **16**, 15188-68-8; **17**, 15259-08-2; **18**, 15188-62-2; **19**, 15188-63-3; **22**, 15188-64-4; **22** acetate, 15259-09-3; **24b**, 15188-65-5; **25b**, 15188-66-6; **27**, 15215-83-5; 1-methylcyclopentene-4-carboxylic acid ethyl ester, 15215-84-6.