Strained Ring Systems. V.[1] The Synthesis of Bicyclo[2.2.0]hexan-2-one and *endo*-Bicyclo[2.2.0]hexan-2-ol

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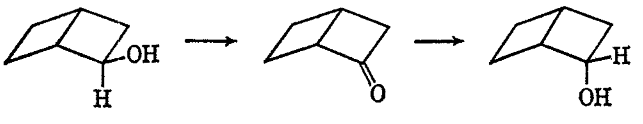
Received August 8, 1966

The major product from Oppenauer oxidation of *exo*-bicyclo[2.2.0]hexan-2-ol (1) is bicyclo[2.1.1]hexan-5-one. Minor amounts of 2-cyclohexenone and *endo*-bicyclo[2.1.1]hexan-5-ol are also produced. *t*-Butyl hypochlorite oxidation of 1 at room temperature gives *exo*-bicyclo[2.2.0]hex-2-yl 5-hexenoate and 5-hexenoic acid, while at 0° bicyclo[2.2.0]hexan-2-one (2) can be observed spectrally and reduced to *endo*-bicyclo[2.2.0]hexan-2-ol with sodium borohydride. Mechanisms of these transformations are discussed. Certain other attempts to prepare 2 are also presented.

The purpose of this paper is to describe our work toward the synthesis of bicyclo[2.2.0]hexan-2-one (2) and *endo*-bicyclo[2.2.0]hexan-2-ol (3) which resulted in the observation of some interesting rearrangements of the bicyclo[2.2.0]hexyl system. The most logical synthesis of *endo*-bicyclo[2.2.0]hexan-2-ol (3) was believed to be the reduction of bicyclo[2.2.0]hexan-2-one (2) with lithium aluminum hydride. Ketone 2 was anticipated as being readily available by oxidation of *exo*-bicyclo[2.2.0]hexan-2-ol (1). Attempts to oxidize *exo*-bicyclo[2.2.0]hexan-2-ol[1] (1) to the corresponding ketone under Oppenauer oxidation conditions resulted in an oxidative rearrangement with bicyclo[2.1.1]hexan-5-one (4) as the major product. Ketone 4 was shown by gas chromatography (gc) integration to be produced in 20% yield (12% isolated yield) along with two minor products which were identified as 2-cyclohexenone (~1% yield) and *endo*-bicyclo[2.1.1]hexan-5-ol (5) (~1% yield). The conditions were those previously employed[3] for the oxidation of 5 to 4 with the reaction time increased to 34 hr. The solvent was ether with quinone as hydrogen acceptor and aluminum *t*-butoxide as catalyst.



1 2 3

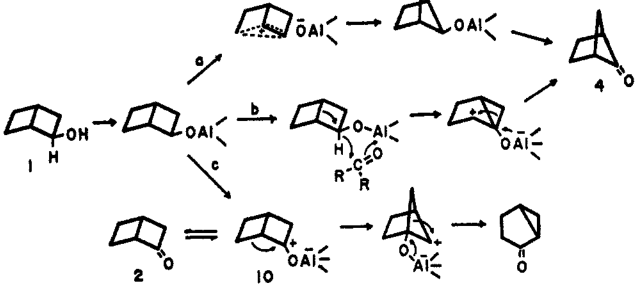
Similar rearrangements under Oppenauer oxidation conditions have been observed for quadracyclanol (6)[4] and cyclopropyl carbinol (8).[5] The oxidative rearrangement of 6 to bicyclo[3.2.0]hepta-3,6-dien-2-one (7) was proposed[4] to proceed by way of the 7-quadracyclylcarbonium ion, formed by loss of hydride from the 7-quadracyclylaluminum alkoxide. It was further observed that aluminum *t*-butoxide alone in refluxing benzene had no effect on quadracyclanone, while under the oxidation conditions quadracyclanone did rearrange to 7. This observation indicates an important function of hydroquinone and quinone in the rearrangement mechanism.

During oxidation of cyclopropylcarbinol (8) to the corresponding aldehyde under Oppenauer conditions with cinnamaldehyde as hydrogen acceptor and aluminum *t*-butoxide as catalyst, small amounts of cyclobutanone were observed in the products.[5] It was found that cyclobutanol was produced in amounts sufficient to account for its observance in the product mixture by treatment of alcohol 8 with only aluminum *t*-butoxide. The mechanism for this rearrangement was proposed to be that in which ionization to a cyclopropylcarbinyl cation–aluminum alkoxide ion pair occurs followed by rearrangement to the cyclobutyl system.

Two mechanisms, therefore, appear reasonable for the oxidative rearrangement of 1 to 4. A mechanism analogous to the rearrangement of 8 would involve dissociation of the aluminum alkoxide of 1 to the bicyclo[2.2.0]hexylcarbonium ion–aluminate ion pair (path a, Scheme I) which with rearrangement, ion pair return, as observed in the acetolysis of the tosylate of 1,[1] and oxidation could lead to the observed ketone 4. In order to test this possibility, 1 was treated with aluminum *t*-butoxide under the oxidation conditions with the exclusion of quinone. If rearrangement were proceeding by path a, sufficient *exo*-bicyclo[2.1.1]hexan-5-ol (9) should be observed to account for the 20% yield of 4. Instead, the starting alcohol 1 was recovered in 50% yield and *endo*-bicyclo[2.1.1]hexan-5-ol (5) was produced in 4–7% yield. This result seems to rule out rearrangement by path a as the principal source of 4. It does, however, explain the observation of the small amount of 5 observed in the oxidation.

SCHEME I

POSSIBLE MECHANISTIC PATHWAYS FOR THE OXIDATIVE REARRANGEMENT OF *exo*-BICYCLO[2.2.0]HEXAN-2-OL UNDER OPPENAUER CONDITIONS



A rearrangement mechanism similar to that proposed for the oxidation of 6 appears most favorable for 1.

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[1] For paper IV in this series, see R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).

[2] This paper comprises a portion of the dissertation submitted by C. E. Reineke to the Graduate School of Kansas State University in April, 1966, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).

[4] P. R. Story and S. R. Fahrenholtz, *ibid.*, **87**, 1623 (1965).

[5] C. C. Lee and I. S. Bhardwaj, *Can. J. Chem.*, **41**, 1031 (1963).

The first step would be formation of the aluminum alkoxide by exchange with aluminum *t*-butoxide. Migration of the 1,4-bridge σ bond of the alkoxide of **1**, with loss of hydride, would lead to a 1-oxybicyclo[3.1.0]hex-2-ylcarbonium ion (path b, Scheme I). The driving force for this rearrangement may be the formation of the more stable cyclopropylcarbinyl cation which has been shown in some instances to exhibit considerable stability.[6,7] Further rearrangement of the bicyclo[3.1.0]hexylcarbonium ion, with the driving force of dissociation of the aluminum alkoxide complex, would give rise to the observed ketone **4**.

To explain the absence of norbornyl-type rearrangement, as observed in the acetolysis of **1** tosylate,[1] it must be that the shift of the 1,4-bridge σ bond to form the bicyclo[3.1.1]hexyl ion occurs simultaneously with the transfer of hydride to the hydrogen acceptor. If this were not the case, it appears that loss of hydride prior to rearrangement (path c, Scheme I) would lead to a bicyclo[2.2.0]hex-2-ylcarbonium ion (**10**) which would correspond to the aluminum *t*-butoxide complex of bicyclo[2.2.0]hexan-2-one (**2**). This ion could also undergo a norbornyl-type rearrangement giving rise to bicyclo[3.1.0]hexan-2-one.

The oxidation of quadracyclanol (**6**) with *t*-butyl hypochlorite (TBH) produced quadracyclanone in 14% yield.[8] Since both compounds **1** and **6** had been demonstrated to be labile under the Oppenauer conditions,[4] it was considered likely that bicyclo[2.2.0]hexan-2-one might be similary produced from **1**. Reaction of **1** with TBH in carbon tetrachloride in the presence of pyridine at room temperature gave two major products. These were identified as 5-hexenoic acid (30% yield) and *exo*-bicyclo[2.2.0]hex-2-yl 5-hexenoate (**11**) (23% yield). The acid was identified by comparison of its infrared spectrum with that of an authentic sample. The structure of **11** was assigned on the basis of spectral data and by reduction with lithium alumium hydride to a mixture of the corresponding alcohols, **1** and 5-hexen-1-ol. The infrared spectrum of **11** exhibited absorptions at 5.75 (C=O), 6.08 (C=C), and 10.95 μ (C=CH$_2$). The nuclear magnetic resonance (nmr) spectrum (carbon tetrachloride, tetramethylsilane internal standard) exhibited absorptions at τ 3.8–4.7, 4.8–5.3, and 8.6–7.1 in a ratio of 1:3:14.5, respectively, which is in agreement with **11**.

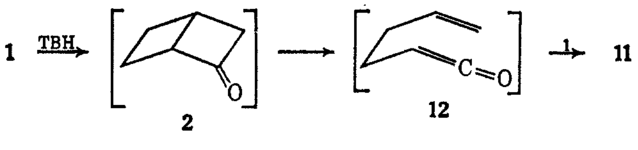
When the reaction of **1** with TBH was performed at 0°, a mixture of products was produced, which exhibited infrared absorption at 5.49 and 5.61 μ. The peaks were encouraging for the presence of a cyclobutanone. The infrared spectrum of a sample of the reaction mixture of another oxidation initially showed a strong, sharp infrared band at 5.61 μ. After about 0.5 hr, additional bands at 5.49 and 5.7–5.8 μ appeared. After 17 hr, a band at 5.75 μ became the major band and the 5.61-μ band had disappeared. Attempts to collect this product by gc shortly after its preparation resulted in the complete disappearance of the 5.61-μ infrared band and partial loss of the 5.49-μ band.

In an attempt to trap the product exhibiting the 5.61-μ carbonyl absorption, the oxidation reaction mixture was immediately reduced with lithium aluminum hydride. There was obtained from this reaction, one major product alcohol identified as 5-hexen-1-ol in 20% yield and unchanged alcohol was recovered in 51% yield. Another oxidation with immediate reduction with lithium aluminum hydride gave a product mixture which showed 20 gc peaks. A major peak from this reaction, with a retention time expected for the starting alcohol **1**, was collected and indicated by the infrared spectrum to be a mixture of *exo-* and *endo*-bicyclo[2.2.0]hexan-2-ol.

A reduction of a TBH oxidation mixture with sodium borohydride gave one major product. This product was identified as *endo*-bicyclo[2.2.0]hexan-2-ol (**3**) in an estimated yield of 10%. The structure of **3** was assigned on the basis of spectral data. The mass spectrum showed a parent peak at *m/e* 98 and a cracking pattern differing only slightly from that of the *exo* isomer **1**.[1] The infrared spectrum showed no unsaturation and was unlike all other possible bicyclic isomers. The nmr spectrum (carbon tetrachloride, tetramethylsilane internal standard) of **3** exhibited a multiplet at τ 5.4–5.9 (C-2 methine hydrogen), a singlet at τ 6.48 (hydroxyl), and continuous absorption from τ 6.7–8.5 (bridgehead methine and methylene hydrogens) in a ratio of 0.65:1:7.3, respectively. The absorption assigned to the C-2 methine is in agreement with that expected by analogy to the norbornyl derivatives[9] and according to the Karplus relationship.

In another reduction of the oxidation mixture with sodium borohydride, no alcohol products were detected. This can be accounted for by the observation of 5-hexenoic acid which would not be reduced by sodium borohydride. Ester **11** would also fail to react with sodium borohydride. That these products were present prior to reduction was indicated by strong infrared absorptions at 5.75 and 5.82 μ, and only weak absorption at 5.61 μ.

The variety of results obtained from the reduction of the TBH oxidation mixtures appear to be explained by the degree of decomposition or rearrangement which occurs prior to reduction. The observance of *endo*-alcohol **3** requires the intermediacy of ketone **2** which appears to correspond to the 5.61-μ carbonyl absorption. The formation of ester **11** is reasonably explained by the spontaneous ring opening of **2** to 4-butenylketene (**12**) which would easily be trapped by **1**. The formation of 5-hexenoic acid can be explained by hydrolysis of either **11** or **12**. Similar ring-opening reactions of some substituted cyclobutenones to ketenes have been previously reported.[10,11]



The apparent ease of rearrangement of **2** compared to the preparation and normal handling of bicyclo[2.1.1]hexan-5-one again point to the greater strain in the [2.2.0] system compared to that in the [2.1.1] system.[1]

Several attempted oxidations of **1** with sodium dichromate and chromic anhydride were characterized by

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(6) K. B. Wiberg and A. J. Ashe, *Tetrahedron Letters*, 4265 (1965).

(7) J. Meinwald and R. A. Schneider, *J. Am. Chem. Soc.*, **87**, 5218 (1965).

(8) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 1270 (1964).

(9) E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).

(10) E. F. Jenny and D. Druey, *J. Am. Chem. Soc.*, **82**, 3111 (1960).

(11) E. F. Jenny and J. D. Roberts, *ibid.*, **78**, 2005 (1956).

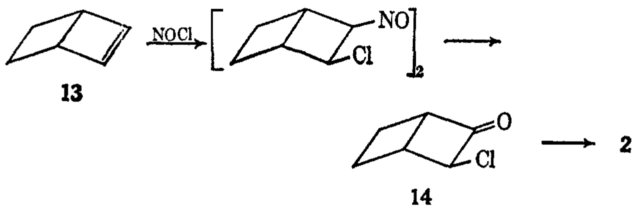
poor yield of product mixtures which exhibited multiple absorptions in the carbonyl region of the infrared spectra. None of the desired ketone 2 could be detected in these reactions.

An oxidation method which failed to produce a reaction with 1 was catalytic oxidation in hexane solution in an oxygen atmosphere with platinum catalyst.[12] This method was successful with cyclohexanol, with oxidation proceeding smoothly to 50% completion in about 8 hr at room temperature. No change was observed on similar treatment of 1 after a total of 24 hr.

An equilibration of the bicyclo[2.2.0]hexan-2-ols was attempted by refluxing the *exo* isomer with fluorenone and sodium in xylene;[13] however, no change in the alcohol was observed.

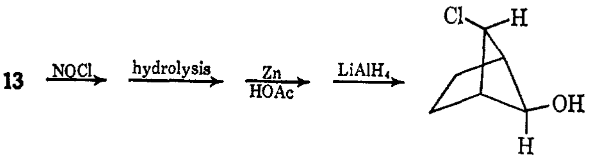
An oxidation method for the conversion of alcohols to aldehydes and ketones with lead tetraacetate in pyridine at room temperature[14] which appeared simple and mild was tested on cyclohexanol and gave cyclohexanone in 58% yield. The loss of the dark red color of the pyridine–lead tetraacetate complex served as an indicator of complete reaction, which for cyclohexanol was after overnight reaction. When this method was applied to 1 the red complex remained for 6 days at room temperature, even after an insured excess of the alcohol was added. The products of this reaction were *exo*-bicyclo[2.2.0]hex-2-yl acetate in 8.3% yield and 5-hexenoic acid in 7.7% yield. Unchanged alcohol (3.7%) was also recovered from the reaction.

A synthetic route to bicyclo[2.2.0]hexan-2-one (2) which was believed to have some promise of success was invisioned in the reaction of bicyclo[2.2.0]hex-2-ene (13) with nitrosyl chloride to produce a nitroso chloride adduct which could be hydrolyzed[15] to the corresponding α-chloro ketone 14. Chloro ketone 14 would then be dechlorinated[16] to produce 2. This sequence of reactions was considered because of the success of this addition to norbornene and other bicyclic olefins to form unrearranged adducts.[15] The conclusion was drawn that these additions, if ionic at all, required very little electron demand of the olefins in the transition state. This sequence of reactions, converting norbornene to 2-norbornanone, was repeated successfully in this work.



The addition of nitrosyl chloride to bicyclo[2.2.0]hex-2-ene (13) produced at least two products. A solid adduct, produced as expected, was found much less stable than the norbornyl adduct, decomposing to a brown isoluble residue upon standing at room temperature and during attempts of recrystallization. The melting point was not sharp, with fusion starting at 85° and ending in decomposition at 130°. The major product of the nitrosyl chloride addition, unlike norbornene, was a blue liquid which also decomposed at room temperature. This product did appear stable indefinitely at −25°.

Levulinic acid hydrolysis of the initially formed solid adduct produced one major product. The infrared spectrum indicated a cyclobutanone structure by strong absorption at 5.50 and 5.55 μ. The nmr spectrum of the crude product showed absorption at τ 8.02 and 6.99 which are characteristic of the methylene and bridgehead methine hydrogens of the bicyclo[2.1.1]hexane system.[17,18] Also the C-6 carbon methylene absorption near τ 8.7 was absent and replaced by a singlet at τ 4.02 which could be attributed to a hydrogen atom attached to a carbon bearing a chlorine atom. A dechlorination reaction on this product with zinc in acetic acid gave a product mixture which was unstable to gc. This mixture gave an nmr spectrum which was similar to the starting mixture. Reduction of this material with lithium aluminum hydride gave two major products in a ratio of 3:1. Both were purified by gc collection and were shown to be alcohols by their infrared spectra. The minor product was not identified. The major product gave an nmr spectrum which exhibited four singlet absorptions at τ 6.01, 6.45, 7.43 and 8.28 in a ratio of 2:1:2:4. On the basis of this data the final product of this sequence of reaction is tentatively assigned the structure of *endo*-6-chloro-*exo*-bicyclo[2.1.1]hexan-5-ol (15). This assignment would require that the methine hydrogens on the carbons bearing the hydroxyl and the chlorine substituents absorb at the same τ value and result in a singlet. Shoolery's effective shieldings[19] for chlorine and hydroxyl are 2.53 and 2.36 ppm, respectively, at least suggesting a similar τ value for these two hydrogens. The nmr spectra of some chlorine-[17] and hydroxyl-substituted[18] bicyclo[2.1.1]hexanes also suggest that it could be possible that these protons absorb at the same τ value.



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From the nmr spectra of the crude products, the rearrangements to the [2.1.1] system occurred either during the addition of nitrosyl chloride to the olefin or during the hydrolysis step of the adduct.

Levulinic acid hydrolysis of the blue liquid adduct proved to be more difficult than the solid adduct, giving incomplete reaction and recovery of some of the nitroso compound. A total of 13 peaks were observed by gc analysis of the crude product and no attempt was made at their further analysis.

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[12] H. Heyns and L. Blazijeniez, *Tetrahedron*, **9**, 67 (1960).

[13] J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Am. Chem. Soc.*, **77**, 3034 (1955).

[14] R. E. Partch, *Tetrahedron Letters*, 3071 (1964).

[15] J. Meinwald, Y. C. Meinwald, and T. N. Baker [*J. Am. Chem. Soc.*, **86**, 4074 (1964)] have recently examined the reaction of NOCl with norbornene.

[16] T. E. Tabor, unpublished results from these laboratories.

[17] J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961).

[18] K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

[19] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry," The Macmillan Co., New York, N. Y., 1959.

Experimental Section

All melting points were taken on a Kofler hot stage and are corrected. Boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer 137 double-beam recording spectrophotometer. Nmr spectra were determined on a Varian A-60 recording spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weights were obtained with a Bendix time-of-flight mass spectrometer. Gc analyses were performed using an F & M Model 500 temperature-programmed gas chromatograph.

Oppenauer Oxidation of *exo*-Bicyclo[2.2.0]hexan-2-ol.—A mixture of 1.0 g (10.2 mmoles) of *exo*-bicyclo[2.2.0]hexan-2-ol,[1] 3.42 g (30.6 mmoles) of benzoquinone, and 2.76 g (11.2 mmoles) of aluminum *t*-butoxide in 125 ml of ether was stirred at room temperature for 34 hr. The dark purple residue was removed by filtration and the yellow filtrate was condensed by distillation of the ether through a 30 cm. Vigreux column to give 1.15 g of crude yellow product. This product was analyzed by gc on a 6 ft × 0.25 in. diisodecyl phthalate column at 100°. Ether and *t*-butyl alcohol were the major components with retention times of 0.71 and 0.82 min, respectively. Four other components were observed with retention times of 3.6, ~5.3 (as a shoulder), ~9 (as a shoulder), and 10.5 min. Ether and *t*-butyl alcohol accounted for 79% of the mixture as found by integration of the peak areas. The other components comprised 17%, <1%, <1, and 3%, respectively, of the total mixture. Each peak was collected by gc from a 15 ft × 0.25 in. diisodecyl phthalate column on which better separation was possible. The component with a retention time of 3.6 min was identified as bicyclo[2.1.1]-hexan-5-one (4) by its infrared[20] and nmr spectra.[18] By integration the yield of this compound was 0.20 g (20%). There was collected from the column 0.12 g (12%) of this compound as a low melting solid.

A sample of the component with a retention time of 5.3 min was collected and the infrared spectrum corresponded well with that of *endo*-bicyclo[2.1.1]hexan-5-ol (5).[20] The yield of this alcohol was less than 10 mg (<1%).

The third component, with retention time of 9 min, gave an infrared spectrum identical with that of 2-cyclohexenone except for a shoulder at 5.8 μ. The yield of this compound was <1% as determined by gc integration.

The component corresponding to the 10.5-min peak was collected from the column as a yellow, crystalline solid and was identified by its infrared spectrum as benzoquinone.

Reaction of *exo*-Bicyclo[2.2.0]hexan-2-ol with Aluminum *t*-Butoxide.—To a stirred solution of 75 mg (0.77 mmole) of *exo*-bicyclo[2.2.0]hexan-2-ol in 10 ml of ether was added 0.21 g (0.84 mmole) of aluminum *t*-butoxide, and the mixture was heated under reflux for 34 hr. The insoluble salts were removed by filtration and the filtrate was condensed by distillation of the ether through a 6-in. vacuum-jacketed Vigreux column to give a residue which showed two components by gc analysis.

The salts from the filtration were hydrolyzed with dilute base by stirring several hours at room temperature in a two-phase ether–water system and the layers were separated. The ether layer was dried and then evaporated to give additional recovery of the two products. The combined residues amounted to 140 mg. This product mixture was analyzed by gc on a 6 ft × 0.25 in. Carbowax 20 M column at 125°. The major components were ether (0.41 min) and *t*-butyl alcohol (0.82 min). Two other components with retention times of 11.9 and 14.8 min were observed. The component with a retention time of 11.9 min comprised 2.3% of the total mixture and was identified as *endo*-bicyclo[2.1.1]hexan-5-ol (5), and the 14.8-min component (starting alcohol) was 25% of the mixture as determined by integration of the gc peak areas. Repeating this experiment gave yields of 4 and 7% of 5.

***t*-Butyl Hypochlorite Oxidation of *exo*-Bicyclo[2.2.0]hexan-2-ol. 1. At Room Temperature.**—The oxidation method used was that described by Grob and Schmid.[21] The *t*-butyl hypochlorite was prepared by the method of Teeter and Bell[22] and the fraction boiling at 78–79° [n^{20}_{D} 1.4021 (lit.[22] bp 77–78°, n^{20}_{D} 1.403)] was used. To a stirred solution of 105 mg (1.07 mmoles) of *exo*-bicyclo[2.2.0]hexan-2-ol and 160 mg (1.6 mmoles) of pyridine in 1 ml of carbon tetrachloride was added dropwise a solution of 95 mg (0.9 mmole) of *t*-butyl hypochlorite in 1 ml of carbon tetrachloride at room temperature. Slight warming of the mixture resulted and a white percipitate of pyridine hydrochloride was produced. An infrared spectrum of a small sample of the reaction mixture was taken after allowing the volatile components to evaporate from the salt plate. A weak carbonyl band at 5.49 μ and strong absorption at 5.75 μ were present. After removal of the solvent by distillation *in vacuo* only the strong absorption band at 5.75 μ remained in the carbonyl region of the infrared spectrum. After standing in a sealed vial at room temperature for 3 months, the crude product gave an infrared spectrum which exhibited an additional carbonyl band at 5.83 μ as a shoulder. Otherwise, the spectrum was not greatly changed. The sample weighed 100 mg. Gc of the sample on a 6 ft × 0.25 in. diisodecyl phthalate column at 175° showed three major components with retention times of 1, 2, and 7 min. Integration of the peak areas showed the peak of retention time of 2 min to be 34% (34 mg) and the peak of retention time of 7 min to be 45% (45 mg) of the total sample. The component with a retention time of 1 min was pyridine as was determined by odor and retention time comparison. The component with a retention time of 2 min was collected from the column and identified as 5-hexenoic acid (30% yield) by its infrared spectrum.

The component with a retention time of 7 min was collected and identified as *exo*-bicyclo[2.2.0]hex-2-yl 5-hexenoate (11), 45 mg (23% yield). The structure was assigned on the basis of the following information: the infrared spectrum and the nmr spectrum (see discussion, p 1889).

On reduction with lithium aluminum hydride, this compound gave a 1:1 mixture of 5-hexen-1-ol and *exo*-bicyclo-[2.2.0]hexan-2-ol. These alcohols were isolated by collection from a 6 ft × 0.25 in. β,β′-oxydipropionitrile column. The infrared spectra were identical with those of the authentic samples. A sample of 5-hexen-1-ol was prepared by hydroboration of biallyl.[23]

2. At Decreased Temperature. A. Without Reduction.—A stirred solution of 100 mg (1.02 mmoles) of *exo*-bicyclo[2.2.0]-hexan-2-ol and 0.16 g (2.0 mmoles) of pyridine in 1 ml of carbon tetrachloride was cooled in an ice bath to 0°. A few drops of solution of 108 mg (1.0 mmole) of *t*-butyl hypochlorite in 1 ml of carbon tetrachloride were added. No reaction was observed, so the ice bath was removed and the mixture was suddenly warmed to 12°. Cooling was continued and the remaining *t*-butyl hypochlorite was added over a period of 12 min. The temperature was not allowed to exceed 10° during the addition. When the addition was complete, the mixture was stirred for 35 min at 0° and the precipitated pyridine hydrochloride was removed by filtration. The colorless filtrate was short path distilled under reduced pressure at room temperature. The distillate, collected in a Dry Ice cooled receiver, showed absorptions in the infrared spectrum at 5.49 (m), 5.61 (s), and 5.70 (sh) μ. After standing overnight in a refrigerator the distillate exhibited diminished infrared absorption at 5.61 μ with the bands at 5.61 and 5.49 μ of nearly equal intensity. The absorption of 5.70 μ had increased and a shoulder at 5.75 μ appeared. The mixture had also turned yellow. Collection of a sample of the total distillate mixture from a 6 ft × 0.25 in. diisodecyl phthalate column gave material which exhibited strong infrared absorption of 5.80 μ and weak absorption at 5.49 μ.

During the gc work, the distillate stood at room temperature for 4 hr. The infrared spectrum after this period showed only weak absorption at 5.61 μ, strong absorption at 5.49 μ, and medium absorption at 5.75 and 5.80 μ.

B. Followed by Reduction with Lithium Aluminum Hydride.—This oxidation was run essentially as described in A above with 175 mg of alcohol. After a total of 1 hr at 2°, 3.5 ml of cold 10% sodium bicarbonate solution was added dropwise and the mixture was stirred at 0–2° for 30 min. The layers were then separated and the aqueous layer was saturated with sodium chloride and extracted twice with small portions of carbon tetrachloride. The combined organic layers were dried over anhydrous sodium sulfate for 15 min, the solutions being kept at 0° at all times. The infrared spectrum of this solution exhibited a strong 5.61-μ band with weak absorption at 5.49, 5.7 (sh), and 5.8 μ.

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(20) Infrared spectra of bicyclo[2.2.1]hexan-5-one and the bicyclo[2.1.1]-hexan-5-ols were kindly provided by Dr. K. B. Wiberg.

(21) C. A. Grob and H. J. Schmid, *Helv. Chim. Acta*, **36**, 1763 (1953).

(22) H. M. Teeter and E. W. Bell, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 125.

(23) G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183 (1962).

Without further processing, this carbon tetrachloride solution was added to a stirred slurry of 0.68 g (17.9 mmoles) of lithium aluminum hydride in 10 ml of tetrahydrofuran cooled in a Dry Ice–isopropyl alcohol bath. The addition required 15 min. The mixture was stirred at this temperature for 1.5 hr and then allowed to warm to room temperature. On warming to room temperature, an exothermic reaction resulted which caused this mixture, which was originally gray, to become reddish brown in color. This was assumed to be the reaction of lithium aluminum hydride with the pyridine present. After 1.5 hr at room temperature the mixture was stirred at 50° for 2 hr and then hydrolyzed with 10 ml of water. Ether was added and the layers were separated. The aqueous layer was saturated with sodium sulfate and extracted with ether. The ether layers were washed once with saturated sodium chloride solution and the solvents were removed by distillation through a 30-cm Vigreux column with the last portions being removed *in vacuo*. The dark red residue was short path distilled *in vacuo* to give 0.24 g of distillate exhibiting strong hydroxyl absorption in the infrared spectrum. Gc analysis on a 6 ft × 0.25 in. β,β'-oxydipropionitrile column at 75° showed two major components with retention times of 15.6 and 24.3 min comprising 14.8 and 37.2%, respectively, of the total mixture.

The peak with retention time of 15.6 min was collected and shown to be 5-hexen-1-ol (35 mg, 20% yield) by comparison of its infrared spectrum with that of an authentic sample. The peak of retention time 24.3 min was *exo*-bicyclo[2.2.0]hexan-2-ol (89 mg, 51% recovery) as shown by the infrared spectrum.

A similar reaction was run in which the oxidation products were not washed with sodium bicarbonate solution, but the pyridinium hydrochloride was removed by filtration. The filtrate was immediately added to a slurry of lithium aluminum hydride at −78° and allowed to react at −78° for 2 hr, then at room temperature for 2.5 hr. The mixture was hydrolyzed with a 40% Rochelle salt solution and the product was isolated as above. Analysis of this product by gc on a Carbowax 20 M column showed 16 peaks. The peaks were collected in groups and analyzed by their infrared spectra. No conclusions could be made on the components with retention times of less than 20 min. A major component with a retention time of 23.2 min was collected and reinjected on the β,β'-oxydipropionitrile column under the conditions described above. The retention time was the same as that of *exo*-bicyclo[2.2.0]hexan-2-ol. The infrared spectrum exhibited peaks characteristic of a mixture of *exo*- and *endo*-bicyclo[2.2.0]hexan-2-ol.

C. **Followed by Reduction with Sodium Borohydride.**—The oxidation products from 200 mg (2.04 mmoles) of *exo*-bicyclo[2.2.0]hexan-2-ol in carbon tetrachloride solution, as produced by procedure A above, were washed with cold 5% sodium bicarbonate solution to remove the pyridine hydrochloride. The infrared spectrum of this washed solution just prior to reduction showed strong absorption at 5.61 μ and only weak absorption at 5.49 and 5.75 μ. The product solution was immediately added to a suspension of 325 mg (8.26 mmoles) of sodium borohydride in 15 ml of absolute ethanol cooled in an ice bath. The addition required about 5 min. A vigorous reaction resulted and the temperature ranged between 10 and 25°. The reaction mixture was stirred at 0° for 30 min and then at room temperature for 2.5 hr. The milky white mixture was hydrolyzed with 10 ml of 10% ammonium chloride solution. The resulting layers were separated and the aqueous layer was saturated with sodium chloride, extracted with methylene chloride, and the combined organic layers were dried over anhydrous sodium sulfate. The solvents were removed by distillation through a 30-cm Vigreux column to give 335 mg of product mixture which was further concentrated to 280 mg of an orange, viscous residue by removing the final traces of solvent *in vacuo* through a 6-in. vacuum-jacketed Vigreux column. The infrared spectrum of this material showed strong absorption at 7.0 and 7.5 μ. This, coupled with the viscous nature of the product, suggested the presence of borate esters. This residue was, therefore, hydrolyzed by stirring at room temperature with 2 ml of 3 *N* sodium hydroxide. The orange solution was acidified with 10% hydrochloric acid and extracted five times with 3-ml portions of pentane. The combined pentane extracts were dried over anhydrous sodium sulfate and the pentane distilled to give 55 mg of a yellow liquid product. This product showed one major component with a retention time of 24.3 min when analyzed by gc on a 6 ft × 0.25 in. β,β'-oxydipropionitrile column at 75°. An estimated 20 μl of this component was collected from the column and characterized as follows. The infrared spectrum showed absorptions at 3.05 (s), 3.43 (s), 3.57 (sh), 6.85 (sh), 6.94 (m), 7.10 (sh), 7.49 (m), 7.85–8 (w), 8.17 (w), 8.59 (s), 9.00 (s), 9.15 (s), 9.31 (s), 9.59 (m), 9.72 (sh), 10.06 (m), 10.65 (m), 11.3 (w), 12.25 (w), 13.05 (w), and 14.0 (w) μ. The mass spectrum showed a parent peak at m/e 98 and a cracking pattern differing only very slightly from that of *exo*-bicyclo[2.2.0]hexan-2-ol.[1] On the basis of this and the nmr data the product was assigned the structure of *endo*-bicyclo[2.2.0]hexan-2-ol (**3**) (~10% yield).

Reaction of *exo*-Bicyclo[2.2.0]hexan-2-ol with Lead Tetraacetate in Pyridine.[14]—A solution of 670 mg (6.83 mmoles) of *exo*-bicyclo[2.2.0]hexan-2-ol and 2.90 g (6.7 mmoles) of lead tetraacetate in 34 ml of pyridine was stirred over night. Since the dark red color of the lead acetate–pyridine complex still remained, another 80 mg of alcohol was added to ensure an excess. After 6 days at room temperature, the red color persisted. The pyridine was removed by distillation under reduced pressure and the dark residue was treated with 20 ml of water. The mixture was extracted three times with 20-ml portions of ether and the combined ether extracts were dried over anhydrous sodium sulfate. After removal at the drying agent, the ether was distilled to give 2.9 g of a dark liquid. The infrared spectrum of this material showed strong absorption as a broad peak of about 5.80 μ. Gc analysis on a 6 ft × 0.25 in. diisodecyl phthalate column at 125° showed two minor components, other than ether and pyridine, at retention times of 5.0 and 7.7 min which comprised 3.7 and 1.6%, respectively, of the total mixture. After standing several months at room temperature in a sealed vial, no change was observed in the infrared spectrum of the product.

A short-path distillation of the material at room temperature and 0.03-mm pressure afforded 0.50 g of a colorless liquid. The infrared spectrum showed the presence of pyridine, strong carbonyl absorption at 5.8 μ and absorption characteristic of an acid from 3 to 4 μ. Analysis of the distillate by gc on a 6 ft × 0.25 in. diisodecyl phthalate column at 125° showed three components with retention times of 4, 5.1, and 9.3 min. Collection of a sample of the total mixture from the column showed no change in the infrared spectrum before and after gc. Pyridine and ether were also present with retention times of less than 2 min.

Each peak was collected from the column and characterized. The peak with a retention time of 4 min corresponded by its infrared spectrum to *exo*-bicyclo[2.2.0]hexan-2-ol (25 mg, 3.7%). The 5.1-min peak, identified by its infrared spectrum, was *exo*-bicyclo[2.2.0]hex-2-yl acetate[1] (80 mg, 8.3% yield). The 9.3-min peak (30 mg) was shown by its infrared spectrum to be an unsaturated acid, $n^{19}\text{D}$ 1.4332. An additional 30 mg of this acid was recovered by further distillation of the pot residue above, giving a total yield of 60 mg. Reduction of this acid with lithium hydride in ether gave an alcohol which identified as 5-hexen-1-ol by comparison of its infrared spectrum with that of an independently synthesized sample. The structure of the acid product was, therefore, 5-hexenoic acid (7.7% yield).

Zinc–Acetic Acid Dechlorination of *exo*-3-Chloronorcamphor.[16]—To a stirred slurry of 1.50 g (4 mmoles) of disodium ethylenediaminetetraacetate dihydrate, 0.66 g (2 mmoles) of sodium acetate, and 0.3 g (2 mmoles) of *exo*-3-chloronorcamphor (from levulinic acid hydrolysis of the NOCl–norbornene adduct)[15] in 2.8 ml of glacial acetic acid was added 0.26 g of zinc powder over a period of 5 min while cooling the mixture in an ice water bath. The mixture was then stirred at room temperature for 2 hr. The excess zinc and insoluble salts were removed by filtration and the reaction flask and salts were washed with 20 ml of ether. The ether solution was treated with saturated sodium bicarbonate solution and then solid bicarbonate was added to the mixture until the aqueous layer was basic to litmus. This mixture was extracted continuously with ether for 16 hr. The ether extract was dried over anhydrous sodium sulfate and, after filtration, the ether was removed by distillation through a 30-cm Vigreux column to yield 0.21 g of crude norcamphor of 90% purity (gc analysis). The yield was 189 mg (86%).

Addition of Nitrosyl Chloride to Bicyclo[2.2.0]hex-2-ene.—A stirred solution of 0.75 g (9.15 mmoles) of bicyclo[2.2.0]hex-2-ene in 10.8 ml of chloroform was cooled in a chloroform–Dry Ice bath at −63°. Nitrosyl chloride (Matheson) was slowly bubbled through the solution which turned light green and then yellowish-brown in color indicating an excess of nitrosyl chloride. Rapid magnetic stirring was maintained while 25 ml of hexane, precooled to −60°, was added. The mixture turned a dark green in color and a solid separated. After stirring at −63° for 30 min, the mixture was allowed to warm to room temperature and the solid material was isolated by centrifugation. The solid was washed with hexane and dried *in vacuo* to give 0.70 g of a light brown solid, mp 85–130°, with decomposition to a black residue occurring at 130°.

The green solution, which remained after removal of the solid product, was condensed *in vacuo* to give a dark blue liquid (0.91 g) which slowly turned green and then brown on standing at room temperature for several days.

In another reaction, carried out in an identical fashion with 1.15 g (14 mmoles) of bicyclo[2.2.0]hex-2-ene, there was obtained 0.62 g of the solid product and 1.57 g of the liquid product. Attempts to recrystallize the solid from chloroform, in which it was only partially soluble, resulted in decomposition to a dark, reddish brown oily residue which was not characterized. The solid alone turned dark brown on standing at room temperature.

The liquid product from this reaction was identical with that obtained above as shown by the infrared spectrum. After standing in a refrigerator at −25°, partial conversion to a colorless, crystalline solid resulted over a period of 4 months. No darkening or loss of blue color of the liquid resulted. A sample of the colorless solid was isolated by washing with carbon tetrachloride and ether. It melted at 70–75° with decomposition to a brown liquid. On cooling to room temperature, the melted sample only partially resolidified. When dissolved in carbon tetrachloride, the solid gave a blue solution.

Levulinic Acid Hydrolysis of Solid Adduct (Above).—The solid product from the addition of nitrosyl chloride to bicyclo[2.2.0]-hex-2-ene (0.70 g, 2.37 mmoles) was stirred at 70–75° for 2.5 hr hr with 15 g of levulinic acid and 1.14 ml of 2 *N* hydrochloric acid. The mixture did not completely clarify during this period. The mixture was added to 50 ml of water and the solution extracted three times with 50-ml portions of ether. The combined ether extracts were washed once with water, three times with 20-ml portions of saturated sodium bicarbonate solution, and dried over anhydrous sodium sulfate. The ether was removed by distillation through a 30-cm Vigreux column with the final traces being removed *in vacuo* to yield an orange liquid containing a small amount of solid material. A short-path distillation of the crude product at room temperature under vacuum gave 0.28 g of a yellow liquid. Gc analysis on a 6 ft × 0.25 in. Carbowax 20 M column at 225° showed three major peaks at retention times of 3.8, 4.5, and 7.1 min in a ratio 1:2.4:11. The nmr spectrum (carbon tetrachloride, tetramethylsilane internal standard) exhibited absorptions at τ 4.02 (singlet), 6.99 (singlet), 7.48 (quartet), and 8.02 (singlet).

There was washed from the distillation head with ether a small amount of solid material which gave weak absorption at 5.50 and 5.55 μ and strong absorption at 5.88 μ with a shoulder at 5.75 μ in its infrared spectrum. This solid material was not further characterized.

Zinc–Acetic Acid Dechlorination of Hydrolysis Product (Above).—To a stirred slurry of the liquid hydrolysis product (0.28 g) from above, 1.59 g (4.28 mmoles) of disodium ethylenediaminetetraacetate dihydrate and 0.70 g (8.56 mmoles) of sodium acetate in 4 ml of acetic acid was added 0.35 g of zinc dust over a period of 5 min while cooling the mixture in an ice bath. The mixture was then stirred at room temperature for 2 hr and the inorganic salts were removed by filtration. The salts were washed with ether and the combined filtrates were treated with saturated sodium bicarbonate solution and solid sodium bicarbonate until the aqueous layer was basic to litmus. The mixture was then continuously extracted with ether for 8 hr. The ether extract was dried over anhydrous sodium sulfate, the sodium sulfate was removed by filtration, and the ether was distilled through a 30-cm Vigreux column to give 0.21 g of crude product. A collection of the total mixture from a Carbowax 20 M column gave matrial which exhibited a totally different infrared spectrum from the material which was injected. The conditions of the column were those given above. The nmr spectrum (neat, tetramethylsilane internal standard) of the crude product showed proton resonance at τ 5.92 (singlet), 7.04 (singlet), and continuous absorption at τ 7.32–9.2 with a sharp peak at τ 8.10.

Lithium Aluminum Hydride Reduction of Attempted Dechlorination Product (Above).—To a slurry of 0.10 g (2.64 mmoles) of lithium aluminum hydride in 10 ml of ether cooled in a Dry Ice–isopropyl alcohol bath was added 4 ml of an ether solution of 0.18 g of the crude dechlorination product from above. The addition required 20 min. The mixture was stirred at −78° for 3.5 hr and then at room temperature for 30 min. The mixture was hydrolyzed by the addition of 1.2 ml of a 40% Rochelle salt solution. The solids were removed by filtration, washed with 20 ml of ether, and the combined ether filtrate and washes were dried over anhydrous sodium sulfate. After removal of the sodium sulfate, the ether was distilled through a 30-cm Vigreux column to afford 120 mg of crude product. Three components were present with retention times on a 12 ft × 0.25 in. diisodecyl phthalate column of 2.0, 4.1, and 9.1 min in a ratio of 1:6.3:17, respectively. Samples of the two major peaks were collected from the gc column under the above conditions. Enough material for a nmr spectrum of the 4.1-min component was not obtained. The infrared spectrum was recorded.

The nmr spectrum (carbon tetrachloride, tetramethylsilane internal standard) of the major component exhibited proton resonance at τ 6.01 (singlet), 6.45 (singlet), 7.43 (singlet), and 8.28 (singlet) in a ratio of 2:1.2:4.

Registry No.—**1**, 3097-64-1; **2**, 10464-68-3; **3**, 10357-70-7; aluminum *t*-butoxide, 556-91-2; *t*-butyl hypochlorite, 507-40-4; lead tetraacetate, 546-67-8; **11**, 10357-65-0; **16**, 10464-71-8; bicyclo[2.2.0]hex-2-ene, 3097-63-0; nitrosyl chloride, 2696-92-6.

Acknowledgment.—The authors wish to express their gratitude to the National Science Foundation (GP-1916 and GP-4888) for support of this research, and for a departmental grant used to purchase the Varian A-60 nmr spectrometer.