Strained Ring Systems. VIII.[1a] An Alternate Synthesis of 2-Oxy Derivatives of Bicyclo[2.2.0]hexane and the Rearrangement of *endo*-Bicyclo[2.2.0]hex-2-yl Acetate[1b]

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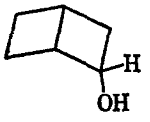
Received February 16, 1968

The synthesis of methyl *endo*-bicyclo[2.2.0]hexane-2-carboxylate (**6**) by diimide reduction of methyl bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (**5**) is reported. Conversion of **6** *via* the methylsulfinyl carbanion and reduction of the resulting adduct leads to a 38:62 mixture of *endo*- (**7**) and *exo*-bicyclo[2.2.0]hex-2-yl methyl ketone (**8**) which on Baeyer–Villiger oxidation yields a mixture of *exo*-bicyclo[2.2.0]hex-2-yl acetate (**9**, 91%), *cis*-bicyclo[3.1.0]hex-2-yl acetate (**10**, 9%), and 3-cyclohexenyl acetate (**11**, <1%). Conversion of **6** into its acid chloride and reaction with dimethylcadmium also gives a mixture of **7** and **8** but in a ratio of 65:35. Baeyer–Villiger oxidation produces a mixture of **9** (49%), *endo*-bicyclo[2.2.0]hex-2-yl acetate (**12**, 27%), **10** (18%), and **11** (6%). On standing in a nonpolar solvent **12** is observed to rearrange to **10** and **11**, thereby establishing them as artifacts of the Baeyer–Villiger reaction. The mechanism of this rearrangement is discussed.

The literature contains relatively few reports of simple functional derivatives of the bicyclo[2.2.0]hexane system.[2] Our reported synthesis of *endo*-bicyclo[2.2.0]hexan-2-ol[2b] (**1**) did not appear attractive for the preparation of the amounts of this alcohol required for solvolytic and other studies. In considering possible alternate routes to **1**, we hoped to synthesize some new monosubstituted derivatives of bicyclo[2.2.0]hexane (as well as **1**) which might be interesting to study in their own right. The present work describes the achievement of certain of these goals. However, *endo* alcohol **1** has been obtained as a mixture with its *exo* epimer which, in our hands, cannot be separated.

The procedure takes advantage of Pettit's elegant conversion of Nenitzescu's *cis*-3,4-dichlorocyclobutene[3] into cyclobutadieneiron tricarbonyl[4–6] (**2**) and its decomposition in the presence of acetylenes to yield substituted bicyclo[2.2.0]hexa-2,5-dienes.[7] Our initial approach to the synthesis of **1** was to attempt to trap the generated cyclobutadiene (from ceric ion oxidation of **2**) with an olefinic substrate. The olefins which we investigated were vinyl acetate, 2-butenone, and methyl acrylate. Each olefin was subjected to the reaction conditions and 2-butenone was found to be very reactive to the ceric ion being immediately converted into polymeric material. Vinyl acetate, although the most stable of these three olefinic compounds to the ceric ion, failed to trap the cyclobutadiene.

Methyl acrylate was intermediate in its stability to the ceric ion. A mixture of products was formed which on column chromatography yielded a substance in 3% yield whose nuclear magnetic resonance (nmr) spectrum was consistent with the expected structure, methyl *endo*-bicyclo[2.2.0]hex-5-ene-2-carboxylate (**3**).[8] Catalytic reduction of **3** gave a 50% yield of at least three products, but no conclusive structural data was obtained.



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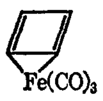

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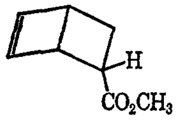

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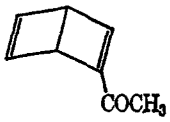

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2-Butynone was found to react with **2** in the presence of the ceric ion to give a mixture of **4** and acetophenone. Attempted gas phase chromatography (gc) of this mixture resulted in quantitative conversion of **4** into acetophenone. Three successive attempts at diimide reduction of this mixture gave a product which by gc analysis showed at least 13 components present.

Rather than fighting this portion of the synthetic sequence further, we turned to the use of methyl propiolate which has already been shown to be a trap for liberated cyclobutadiene.[7] In our hands a 49% yield of a mixture of methyl bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (**5**) (71% of the mixture) and methyl benzoate (29% of mixture) was obtained. Attempted gc analysis or catalytic reduction with Adams catalyst gave quantitive conversion into methyl benzoate. Diimide reduction[9] of this mixture containing **5** gave a product in 52% yield (based on available **5**) which is assigned the structure of methyl *endo*-bicyclo[2.2.0]hexane-2-carboxylate (**6**) from analysis of its nmr spectrum, its subsequent conversions, and analogy with diimide reductions in other bicyclic olefins.[10] The yield is based on the amount of **5** present in the mixture from the nmr integration. The mass spectrum of the ethyl ester of **6** showed the parent ion at *m/e* 154 with the base peak at *m/e* 81 corresponding to loss of the carboethoxy group. Ester **6** was found to be epimerized by methanolic sulfuric acid, but not when treated with methanolic sodium methoxide.

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(1) (a) For paper VII in this series, see R. N. McDonald and D. G. Frickey, *J. Amer. Chem. Soc.*, **90**, 5315 (1968). (b) A portion of this research was communicated in *Tetrahedron Lett.*, 1449 (1968). (c) Taken from the M.S. thesis of G. E. Davis.

(2) Although there are a number of reports of substituted bicyclo[2.2.0]hexanes highly alkylated or involved in higher polycyclic molecules, we have been concerned with mono- and disubstituted derivatives of the [2.2.0] ring system. These are (a) *exo*-2-ol, its acetate, and tosylate [R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967)]; (b) *endo*-2-ol and 2-one [*ibid.*, 1888 (1967)]; (c) 1- and *exo*-2-chloride [R. Srinivasan and F. I. Sonntag, *Tetrahedron Lett.*, 603 (1967)]; (d) 1,4-dichloride [W. Luettke and V. Schabacker, *Ann.*, **698**, 86 (1966)]; (e) 4-chloro-1-bromide (K. V. Scherer, Abstracts of the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P180); (f) 4-chloro-1-carboxylic acid, its methyl ester, 4-chloro-1-methanol, and 1-methanol and its *p*-nitrobenzoate [W. G. Dauben, J. L. Chitwood, and K. V. Scherer, *J. Amer. Chem. Soc.*, **90**, 1014 (1968)]; (g) *cis*-2,3-dicarboxylic acid and its anhydride.[2a]

(3) M. Avram, I. Dinulescu, M. Elian, M. Farcasiu, E. Marica, G. Mateescu, and C. D. Nenitzescu, *Ber.*, **97**, 372 (1964).

(4) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965).

(5) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967).

(6) M. Rosenblum and C. Gatsonis, *ibid.*, **89**, 5074 (1967).

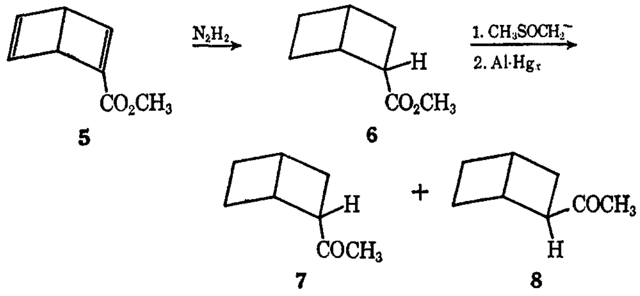
(7) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

(8) The analogy with the exclusive formation of dimethyl *cis,endo*-bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylate from similar treatment of **2** in the presence of dimethyl maleate [L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **88**, 623 (1966)] supports the assignment of the *endo* configuration of the carbomethoxy group in **3**.

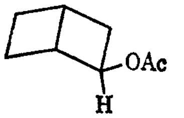
(9) E. E. van Tamelen and S. P. Pappas [*ibid.*, **85**, 3297 (1963)] have reported that diimide reduces bicyclo[2.2.0]hexa-2,5-diene to bicyclo[2.2.0]hexane.

(10) P. G. Gassman and J. M. Hornback, *ibid.*, **89**, 2487 (1967); E. E. van Tamelen and R. J. Timmons, *ibid.*, **84**, 1067 (1962); C. E. Miller, *J. Chem. Educ.*, **42**, 254 (1965).

Reaction of methylsulfinyl carbanion[11] with **6** was considered to be a convenient route to *endo*-bicyclo[2.2.0]hex-2-yl methyl ketone (**7**). When this reaction was carried out on crude **6** (containing some methyl benzoate), a mixture of two adducts was formed. The white solid adduct was shown to be ω-(methylsufinyl)-acetophenone by comparison with that reported.[11] The second adduct, a yellow oil, was then reduced with aluminum amalgam to ketonic products. The nmr spectrum of this product indicated it to be a mixture of **7** and the *exo* ketone **8** since two distinct methyl singlets are present. From the results of subsequent conversions of this mixture, an alternate synthesis of a mixture of **7** and **8**, and the results of its further reactions, we assign the τ 8.20 absorption to the *exo* epimer **8** and that of the *endo* epimer **7** at 8.13. Using these assignments the mixture produced by this route contains **7** and **8** in a ratio of 38:62.[12]



Baeyer–Villiger oxidation of this mixture of ketones **7** and **8** with *m*-chloroperbenzoic acid resulted in a mixture of acetates which exhibited two peaks on gc analysis. The major gc peak was identified as *exo*-bicyclo[2.2.0]hex-2-yl acetate (**9**, 91%), and the minor peak as a mixture of *cis*-bicyclo[3.1.0]hex-2-yl acetate (**10**, 9%) and 3-cyclohexenyl acetate (**11**, <1%).



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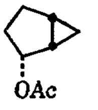

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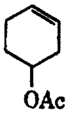

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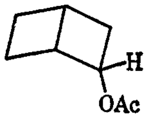

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The percentage composition of this mixture is derived from a combination of nmr spectral and gc integrations.

Since none of the desired *endo*-bicyclo[2.2.0]hex-2-yl acetate (**12**) was produced, the more classical method of converting an acid into its methyl ketone was investigated. Saponification of ester **6** and conversion into its acid chloride were found to proceed without isomerization.[13] Treatment of the acid chloride with dimethylcadmium produced a mixture of ketones **7** and **8**, but with **7** in predominance, in a ratio of 65:35. After standing for 40 days stored in Dry Ice the ratio had changed to 51:49. It was first assumed that magnesium halide present in the dimethylcadmium reagent had caused the isomerization of **7** to **8**, but the use of magnesium halide free dimethylcadmium[14] gave a similar result.[15] *m*-Chloroperbenzoic acid oxidation of the 51:49 mixture of **7** and **8** led to a mixture of acetates again showing only two major peaks on gc analysis. The first of these gc peaks was collected and identified by infrared (ir) and nmr spectroscopy as a mixture of acetates **9** (49%) and **12** (27%) while similar identification of the second peak showed it to consist of acetates **10** (18%) and **11** (6%).[16] Monoperphthalic acid oxidation of a portion of the 65:35 mixture of ketones **7** and **8** also give a mixture of **9** (40%), **10** (32%), **11** (9%), and **12** (19%), however, in somewhat different proportions.

Lithium aluminum hydride reduction of the product from the Baeyer–Villiger oxidation utilizing *m*-chloroperbenzoic acid gave a mixture of alcohols in 82% yield which showed four peaks on gc analysis. The first peak (72.2% of the mixture by weight) was collected and identified as a mixture of **1** and its *exo* epimer, *exo*-bicyclo[2.2.0]hexan-2-ol, by comparison of the ir and nmr spectra and gc retention times with those of authentic samples, in a ratio of 36:64, respectively.[17] All attempts to separate these isomers failed. The second gc peak (12.5% of the mixture) was collected and similarly identified as *cis*-bicyclo[3.1.0]hexan-2-ol. The third (5.2%) and fourth (10.1%) peaks were collected but no positive identification was made.

Acetates **10** and **11** were prepared by Simmons–Smith reaction with 2-cyclopentenol[18] followed by acetylation and were found to be identical with the products in the second gc fraction. To establish that none of the acetate of *trans*-bicyclo[3.1.0]hexan-2-ol was a product, it was synthesized by oxidation of the *cis* alcohol, Meerwein–Ponndorf reduction of the ketone to an 88:12 mixture of *trans*- and *cis*-bicyclo[3.1.0]-hexan-2-ols,[19] and acetylation. The acetate, *trans*-bicyclo[3.1.0]hex-2-yl acetate, was found to be different from any of the rearrangement products. Acetates **10**, **11**, and *trans*-bicyclo[3.1.0]hex-2-yl acetate were found to be stable to the Baeyer–Villiger reaction conditions. *exo* acetate **9** had been previously shown to be stable to acetolysis at 90° [2a] and its stability was assumed in the present case as well.

The question of how acetates **10** and **11** were being produced in the Baeyer–Villiger oxidations was answered by observing the change in the nmr spectrum of a sample of the first gc fraction containing acetates **9** and **12** in a ratio of 46:54. After storage in carbon tetrachloride solution at −26° for 21 days, the composition had changed to 46% **9**, 22% **12**, 25% **10**, and 7% **11** by nmr integration. After being stored for an additional 25 days in methylene chloride, the product composition had changed further to 46% **9**, 14% **12**, 31% **10**, and 9% **11**.

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(11) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

(12) In the conversion of **6** into the mixture of **7** and **8**, it is believed that the isomerization occurs in the aluminum amalgam reduction since the nmr spectrum of the **6**-methylsulfinyl carbanion adduct suggests the presence of only one isomer.

(13) The acid was reconverted into **6** with diazomethane and the acid chloride was hydrolyzed to the acid.

(14) J. Cason, *ibid.*, **68**, 2078 (1946).

(15) See K. B. Wiberg and B. A. Hess, *J. Org. Chem.*, **31**, 2250 (1966), for a discussion of related isomerizations.

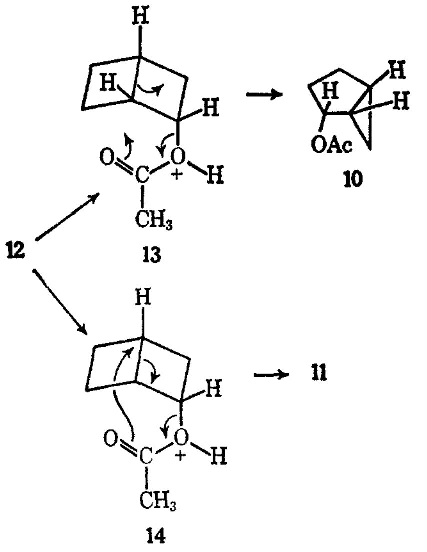
(16) The reasons for the quite different results in the Baeyer–Villiger oxidations with *m*-chloroperbenzoic acid are unknown, but it should be pointed out that the concentrations of peroxy acid and visual appearances of the two reactions were different.

(17) This ratio of *exo* and *endo* alcohols was obtained by integration of the nmr spectrum of the original acetate mixture.

(18) E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, **85**, 1782 (1963), using a zinc-copper couple prepared according to R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

(19) We employed a relatively short reaction time in order to produce this mixture rich in the *trans* alcohol; see M. Hanack and H. Allmendinger, *Ber.*, **97**, 1669 (1964), for the use of longer reaction times giving a *cis*/*trans* ratio of 38:62.

From the facts that the rearrangement produces only *cis* acetate **10** and **11**[20] and the low polarity of the media,[21] we suggest that the rearrangement of **12** to **10** proceeds by an acid-catalyzed, concerted mechanism, *i.e.*, structure **13**. Since acetates **9** and **10** do not rearrange to give **11**, this acetate must also arise directly from **12** in either a concerted process or one which incorporates a tight ion pair. A concerted mechanism in going from **12** to **11** may be questionable owing to the rather extensive steric crowding in the *endo* face of the molecule by migration of the acetoxy group to C4 (structure **14**). Rearrangement from the [2.2.0] to the [3.1.0] system would be favored by about 18 kcal/mol based on simple strain energy considerations.[22]



Experimental Section[23]

***cis*-3,4-Dichlorocyclobutene.**—The procedure used starting with cyclooctatetraene[24] has been described.[3] From an average run with 83.2 g of cyclooctatetraene there was obtained 5.9 g (5.4%) of *trans,trans*-1,4-dichlorobutadiene, bp 60° (60 mm) [lit.[3] bp 60° (68 mm)], and 30.0 g (31%) of *cis*-3,4-dichlorocyclobutene, bp 74° (58 mm), $n^{25.5}$D 1.4983 [lit.[3] bp 74° (60 mm), n^{25}D 1.49832]. The ir and nmr spectra were in agreement with these structures.

Diiron Enneacarbonyl.—This compound was prepared by a modification of the method of Speyer and Wolf.[25] Iron pentacarbonyl (200 g, 1.02 mol) in 410 ml of glacial acetic acid was maintained under a nitrogen atmosphere while being irradiated with a GE-AH4 uv lamp (with the Pyrex envelope removed) in a quartz, water-cooled well. At the end of 37 hr, the solid product was filtered from the reaction mixture, washed repeatedly with anhydrous ether, and air dried (100.9 g). The mother liquor (without ether) was irradiated for another 70.6 hr and the golden crystals were worked up as before (42.7 g). The total yield was 143.6 g (81%) with a total reaction time of 107.6 hr. Dry diiron enneacarbonyl is stable toward oxygen and moisture, but burns spontaneously in the air if moistened with iron pentacarbonyl.

Cyclobutadieneiron Tricarbonyl (2).—To a solution of 28.0 g (0.23 mol) of *cis*-3,4-dichlorocyclobutene in 980 ml of pentane heated under reflux (bath temperature 47–48°) and a nitrogen atmosphere was added 171.0 g (0.470 mol) of diiron enneacarbonyl in portions over a 20-hr period. After heating for an additional 3 hr, the reaction mixture was cooled to room temperature and the deep green liquid was filtered under a nitrogen atmosphere from the solid residue. The solvent and iron pentacarbonyl were removed from the complex by trap-to-trap distillation at reduced pressure. The product distilled as a yellow-green liquid (21.05 g, 48%) at 27° (0.05 mm) [lit. 40%, bp 68–70° (3 mm),[4] and 51%, bp 45–47° (3 mm)[5]] and solidified to a yellow-green solid when cooled below room temperature. This complex slowly decomposes in the presence of air or moisture to give a reddish brown solid insoluble in water and most organic solvents.

Methyl *endo*-Bicyclo[2.2.0]hex-5-ene-2-carboxylate (3).—Ceric ammonium nitrate (10.0 g, 18.2 mmol) in 22 ml of water was added over a 15-min period to a solution of cyclobutadieneiron tricarbonyl (1.0 g, 5.2 mmol) and methyl acrylate (4.49 g, 52 mmol) in 40 ml of 95% ethyl alcohol. The reaction mixture was maintained at 0 to −2°. Bubbles were given off during the addition of the ceric ion solution. The reaction mixture was extracted with six 20-ml portions of ether, the combined ether extracts were washed with several portions of water, and the resulting solution was dried over magnesium sulfate. The concentrated reaction mixture was chromatographed on silica gel. The fraction which eluted with 1:1 ether, methylene chloride was trap-to-trap distilled [27° (0.05 mm] to yield a clear, colorless liquid (0.02 g, 3%). The nmr spectrum [$CDCl_3$, internal tetramethylsilane (TMS)] exhibited absorptions at τ 3.58 (multiplet, 2) and 6.0–8.17 (continuous absorption, 8) with a singlet at 6.25.

Bicyclo[2.2.0]hexa-2,5-dien-2-yl Methyl Ketone (4).—Ceric ammonium nitrate (10.0 g, 18.2 mmol) in 22 ml of distilled water was added to a mixture of cyclobutadieneiron tricarbonyl (1.0 g, 5.2 mmol) and 2-butynone (1.77 g, 26.0 mmol) in 40 ml of 95% ethanol. The reaction was maintained at −1 to −3° during an addition time of 70 min. After the addition the solution was stirred for another 30 min and 0.2 g of ferrous ammonium sulfate was added. This mixture was stirred an additional 10 min and extracted with five 40-ml portions of ether, and the ether was washed with five 40-ml portions of water. The resulting ether extract was dried, concentrated at reduced pressure, and trap-to-trap distilled [27° (0.05 mm)] to yield 0.17 g (27%) of a light yellow liquid. Gc analysis of this product on a 6 ft × 0.25 in. Carbowax 20M column (20% on Chromosorb W) at a temperature of 175° showed one major peak which when collected proved to be acetophenone.

From the nmr spectrum (CCl_4, internal TMS) of the product it is estimated to be composed of **4** and acetophenone in a ratio of 3:1. The nmr absorptions attributed to **4** appear at τ 2.98 (multiplet, 1), 3.44 (multiplet, 1), 3.54 (multiplet, 1), 6.08 (multiplet, 1), 6.21 (multiplet, 1), and 7.89 (singlet, 3).

Methyl Bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (5).—Ceric ammonium nitrate (50.0 g, 91 mmol) in 110 ml of distilled water was added to a mixture of cyclobutadieneiron tricarbonyl (5.4 g, 28 mmol) and methyl propiolate (21.9 g, 0.26 mol) in 200 ml of 95% ethanol. The reaction was maintained at −1 to −3° during an addition time of 1.5 hr. After the addition, the solution was stirred for another 15 min and 0.2 g of ferrous ammonium sulfate was added. This mixture was stirred an additional 10 min and extracted with five 40-ml portions of ether, and the combined ether extracts were washed with five 40-ml portions of water. After drying and concentration under reduced pressure, the residual material was trap-to-trap distilled [26° (0.01 mm)] to yield 3.0 g of a light yellow liquid. Gc analysis of this product on a Carbowax 20M column (20% on Chromosorb W) showed two major components to be present; the first was identified as methyl propiolate and the second as methyl benzoate (45% of product mixture). From the inte-

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[20] P. K. Freeman, M. F. Grostic, and F. A. Raymond [*J. Org. Chem.*, **30,** 771 (1965)] have reported that the *p*-toluenesulfonic acid catalyzed addition of methanol to bicyclo[3.1.0]hex-2-ene yields a mixture of *trans*- (53%) and *cis*-2-methoxybicyclo[3.1.0]hexanes (32%) and 4-methoxycyclohexene (15%).

[21] R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail [*J. Amer. Chem. Soc.*, **89,** 880 (1967)] observed a rearrangement of β-(*syn*-7-norbornenyl)-methyl brosylate in unbuffered carbon tetrachloride, but not in the buffered solvent.

[22] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley & Sons, Inc., New York, N. Y., 1965, p 193.

[23] All boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 double-beam recording spectrophotometer and nmr spectra were determined on a Varian A-60 recording spectrometer. The mass spectrum was obtained with a Bendix time-of-flight mass spectrometer. The gas chromatographic analyses were performed using a F & M Model 500 high temperature programmed gas chromatograph. Analyses were performed by Gailbraith Laboratories, Inc., Knoxville, Tenn.

[24] We wish to thank BASF-AG for a generous sample of cyclooctatetraene.

[25] E. Speyer and H. Wolf, *Ber.*, **60,** 1424 (1927).

grated nmr spectrum of the mixture, 71% of the methyl benzoate from the gc analysis originally was 5 and 29% was methyl benzoate. From these values, the mixture of 5 and methyl benzoate was obtained in 49% yield.

Methyl *endo*-Bicyclo[2.2.0]hexane-2-carboxylate (6).—Glacial acetic acid (12.65 ml, 13.26 g, 0.222 mol) in 30 ml of methanol was added under nitrogen to a mixture of potassium azodicarboxylate [prepared from 9.32 g (0.111 mol) of azodicarbonamide] and the previous mixture containing methyl bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (2.90 g, 21.4 mmol)[26] in 200 ml of methanol and 50 ml of water. The addition was complete after 3.5 hr. The resulting mixture was stirred for an additional 4 hr and added to 500 ml of ether. The ether solution was washed with eight 100-ml portions of water, dried, concentrated under reduced pressure, and trap-to-trap distilled [27° (0.05 mm)] to yield 2.54 g. The integrated nmr spectrum indicated that this product mixture was composed of 52% **6**, 28% methyl benzoate, and 20% methyl propiolate; the amount of **6** present was 1.56 g (52%). The combined products from four such runs were distilled through a 30-cm spinning-band column [81° (60 mm)] to yield 4.5 g of **6** (>95% pure by nmr analysis). The over-all yield from **2** was 20%.

The ir spectrum of **6** (gc collected) exhibited absorptions at 5.77 (C=O) and 8.30 μ (C—O). The nmr spectrum (CCl$_4$, internal TMS) showed a singlet absorption at τ 6.4 with almost continuous absorption from 6.24 to 8.32 in a ratio of 3:8.3.

Anal. Calcd for C$_8$H$_{12}$O$_2$: C, 68.55; H, 8.63. Found: C, 68.67; H, 8.82.

In a single run using ethanol instead of methanol as solvent, the corresponding ethyl esters were isolated.

Attempted Base Equilibration of Methyl *endo*-Bicyclo[2.2.0]hexane-2-carboxylate.—Methyl *endo*-bicyclo[2.2.0]hexane-2-carboxylate (50 mg), sodium metal (5 mg), and 0.3 ml of anhydrous methanol were stirred together for 48 hr at room temperature. At the end of this period the reaction mixture was added to 5 ml of water, extracted with four 10-ml portions of ether, dried over magnesium sulfate, concentrated at reduced pressure, and trap-to-trap distilled [27° (0.05 mm)] to yield 10 mg of a clear, colorless liquid. An nmr spectrum identified this as the starting *endo* ester. The aqueous portion from the reaction work-up was acidified with dilute hydrochloric acid, extracted with ether, dried, and esterified with diazomethane. An nmr spectrum of the resulting ester (30 mg) proved to be identical with that of the starting *endo* isomer.

Acid Equilibration of Methyl *endo*-Bicyclo[2.2.0]hexane-2-carboxylate.—Methyl *endo*-bicyclo[2.2.0]hexane-2-carboxylate (30 mg), 6 ml of anhydrous methanol, and 4 drops of concentrated sulfuric acid were stirred together for 13 days at room temperature. At the end of this period the reaction mixture was diluted with 20 ml of ether, washed with three 10-ml portions of water, dried, concentrated at reduced pressure, and trap-to-trap distilled [27° (0.05 mm)]. The clear, colorless distillate was analyzed by gc and found to have the same retention time as the starting *endo* ester **5**. A mixture of the distillation product and the starting ester gave a single peak. The ir and nmr spectra for this product and **5** showed distinct differences, although similarities were evident. The extent of equilibration is uncertain but is assumed to be high from considerations of the spectra.

Bicyclo[2.2.0]hex-2-yl Methylsulfinylmethyl Ketone.—To a stirred solution of the methylsulfinyl carbanion [prepared from 0.556 g (10 mmol) of 44% sodium hydride suspension and 1.3 ml of dimethyl sulfoxide] in 1.3 ml of tetrahydrofuran[11] cooled in an ice bath under nitrogen was added 0.65 g (4.7 mmol) of ester **6** (containing some methyl benzoate) over a 10-min period. Stirring at room temperature was continued for 1 hr followed by the addition of 7.8 ml of water and the mixture was acidified to pH 3 with dilute hydrochloric acid. This was extracted with three 40-ml portions of chloroform and the combined extracts were washed with three 20-ml portions of water, dried, and concentrated at reduced pressure to yield 0.86 g (>95% yield) of a yellow oil. Trituration of this oil with cold isopropyl ether and ethyl ether produced 0.28 g of a white solid and 0.58 g of yellow oil. The solid was identified by its nmr spectrum as ω-(methylsulfinyl)acetophenone derived from methyl benzoate. The ir spectrum of the yellow oil exhibited absorptions at 5.90 (C=O) and 9.60 (S=O) μ while the nmr spectrum (CDCl$_3$, internal TMS) showed absorptions at τ 6.2 (singlet, 2), 7.29 (singlet, 3), and continuous absorption at 6.08–8.32 (9 H).

Aluminum Amalgam.—Strips (~10 cm × 1.0 cm) of aluminum foil (0.83 g, 31 mg-atoms) were rinsed with absolute alcohol and anhydrous ether, immersed in a saturated, aqueous mercuric chloride solution for 45 sec, rinsed with absolute alcohol followed by anhydrous ether, and used immediately in the following reaction.[27]

Reduction of Bicyclo[2.2.0]hex-2-yl Methylsulfinylmethyl Ketone.—The strips of aluminum amalgam prepared above were cut into small pieces and added to a solution of 0.58 g (3.0 mmol) of the sulfinylmethyl ketone in 36 ml of 90% aqueous tetrahydrofuran. The reaction mixture was stirred under reflux for 2 hr, cooled, filtered from the solid residue, and concentrated by distillation of the solvent through a 30-cm Vigreux column. The concentrated product mixture was added to 250 ml of ether, dried over magnesium sulfate, concentrated, and trap-to-trap distilled to yield 0.20 g (85%) of a clear, colorless liquid, bp ~27° (0.05 mm). Gc analysis on a Carbowax 20M column showed only one major peak which was collected. The ir spectrum of this peak showed a single, sharp carbonyl absorption at 5.88 μ and the nmr spectrum (CCl$_4$, internal TMS) exhibited continuous absorption at τ 6.41–8.32 with methyl singlets at 8.02 and 8.13. From the integration and factors presented in the discussion section, this gc peak is assigned the composition of *endo*- (**7**) and *exo*-bicyclo[2.2.0]hex-2-yl methyl ketones (**8**) in the ratio of 38:62.

***Baeyer–Villiger Oxidation of the 38:62 Mixture of Ketones* 7 *and* 8.**—The mixture of ketones **7** and **8** (0.19 g, 1.5 mmol) prepared as described above and 0.37 g (2.1 mmol) of 80% *m*-chloroperbenzoic acid in 2.8 ml of methylene chloride was allowed to stir at room temperature for 3 days. The reaction mixture was diluted with 10 ml of methylene chloride, washed with two 5-ml portions of 10% sodium hydroxide, two 2-ml portions of water, two 5-ml portions of 10% sodium bisulfite, and 3 ml of water. The organic layer was dried, concentrated, and trap-to-trap distilled through a short-path column [27° (0.05 mm)] to give 0.19 g (89%) of a clear, colorless liquid. Gc analysis on a Carbowax 20M column showed two peaks, the first of which was collected and proven to be *exo*-bicyclo[2.2.0]hex-2-yl acetate by comparison of its nmr spectrum with that of authentic material.[2a] This comprised 91% of the product mixture.

The second gc peak was collected and identified as a mixture of *cis*-bicyclo[3.1.0]hex-2-yl acetate (9% of product mixture) and 3-cyclohexenyl acetate (<1% of product mixture) by nmr spectral comparisons with the spectra of authentic samples. No indication of the presence of *endo*-bicyclo[2.2.0]hex-2-yl acetate could be found.

***endo*-Bicyclo[2.2.0]hexane-2-carboxylic Acid.**—Methyl *endo*-bicyclo[2.2.0]hexane-2-carboxylate (4.5 g, 32 mmol) and potassium hydroxide (3.62 g, 65 mmol) were combined in 21 ml of dry methanol and heated under reflux for 2.3 hr. The reaction mixture was added to 60 ml of water (0°), washed with three 50-ml portions of ether, acidified with concentrated hydrochloric acid, and extracted with six 50-ml portions of ether. This extract was dried, concentrated at reduced pressure, and trap-to-trap distilled [60° (0.005 mm)] to yield 4.0 g (98%) of a clear, colorless liquid. The ir spectrum was in agreement with the assigned structure and the nmr spectrum exhibited absorptions at τ 1.33 (singlet, 1) with continuous absorption at 6.25–8.41 (10.6 H).

Treatment of a portion of the acid with ethereal diazomethane gave the corresponding methyl ester, the ir spectrum of which was identical with that of starting *endo* ester **6**.

***endo*-Bicyclo[2.2.0]hexane-2-carbonyl Chloride.**—*endo*-Bicyclo[2.2.0]hexane-2-carboxylic acid (4.0 g, 32 mmol), thionyl chloride (7.6 g, 64 mmol), and 1 drop of dimethylformamide were combined under a nitrogen atmosphere, stirred at room temperature for 1 hr, and heated under reflux for 4 hr. The excess thionyl chloride was removed under reduced pressure and the product was trap-to-trap distilled at 27° (0.05 mm) to yield 4.2 g (90%) of the desired acid chloride as a clear, colorless liquid.

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(26) This amount of **5** is based on the above integrated percentages in its preparation since the crude mixture was employed in this reduction.

(27) Little success was observed using a 2% mercuric chloride solution and shorter times for the amalgamation process described in ref 11.

A portion of the acid chloride was hydrolyzed to an acid whose ir spectrum was identical with that of the starting *endo* acid.

exo- (**8**) **and** *endo*-**Bicyclo[2.2.0]hex-2-yl Methyl Ketone (7).**—The above acid chloride (4.20 g, 29 mmol) in 15 ml of benzene was added slowly with cooling to a solution of distilled [25° (0.1 mm)] dimethylcadmium[14] (prepared from 16.3 g of methyl bromide, 3.1 g of magnesium, and 12.7 g of cadmium chloride) in 20 ml of benzene. At the end of the addition the mixture was stirred an additional 2 hr. at room temperature under a nitrogen atmosphere. A saturated solution of ammonium chloride was slowly added, the layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed twice with water, dried, and concentrated under reduced pressure. Trap-to-trap distillation at 27° (0.05 mm) gave 1.85 g (51%) of a clear, colorless liquid. Gc analysis showed one major component whose ir and nmr spectra were similar to those of the mixture of ketones **7** and **8** previously obtained. However, in this case *endo* ketone **7** was predominant in a ratio of 65:35 (from comparison of the methyl singlet peak heights in the nmr spectrum). After 40 days at Dry Ice temperature, this ratio of **7** and **8** had changed to 51:49.

Baeyer–Villiger Oxidations of the Mixture of Methyl Ketones 7 and 8. A. Using *m*-**Chloroperbenzoic Acid.**—The 51:49 mixture of ketones **7** and **8** (1.80 g, 14.5 mmol) and 10.33 g (48.4 mmol) of 80% pure *m*-chloroperbenzoic acid in 65 ml of methylene chloride was allowed to react as previously described to yield, after work-up, 1.81 g (89%) of a clear, colorless liquid. The integrated nmr spectrum of this product showed it to be a mixture of acetates **9** (49%), **10** (18%), **11** (6%), and **12** (27%).

In a smaller run using 47 mg (0.4 mmol) of a 71:29 mixture of **7** and **8**, a 90% yield of acetates was obtained composed of 35% **9**, 17% **10**, 6% **11**, and 42% **12**. The rearrangements of this product mixture in carbon tetrachloride and methylene chloride are presented in the discussion section.

B. Using Monoperphthalic Acid.—The 65:35 mixture of ketones **7** and **8** (86 mg, 0.69 mmol) and 0.29 g (1.59 mmol) of monoperphthalic acid in 4.5 ml of ether was stirred at room temperature for 2 hr. The reaction mixture was diluted with 10 ml of ether, washed with two 3-ml portions of 10% sodium hydroxide solution followed by two 2-ml portions of water, two 3-ml portions of 10% sodium bisulfite solution, and finally 3 ml of water. The organic layer was dried and concentrated, and the residue was trap-to-trap distilled [27° (0.05 mm)] to give 80 mg (83%) of a clear, colorless acetate mixture. Integrated nmr spectral analysis showed this produce to contain 40% **9**, 32% **10**, 9% **11**, and 19% **12**.

Lithium Aluminum Hydride Reduction of the Mixture of Acetates Obtained from Baeyer–Villiger Oxidation Procedure A.—The mixture of acetates obtained in procedure A above (1.81 g, 12.9 mmol) dissolved in 40 ml of anhydrous ether was added over a 15-min period to a suspension of 1.0 g (26.4 mmol) of lithium aluminum hydride in 50 ml of anhydrous ether. The mixture was heated under reflux for 6 hr, cooled in an ice bath, and carefully hydrolyzed with water. The layers were separated. The aqueous layer was extracted with two 50-ml portions of ether, then acidified with concentrated hydrochloric acid, and further extracted with three 75-ml portions of ether. The latter ether extracts were combined, dried, concentrated, and trap-to-trap distilled [24° (0.02 mm)] to yield 1.04 g (82%) of a clear, colorless liquid. Gc analysis of this product on a 12 ft × 0.25 in. β,β'-oxydipropionitrile column (10% on Chromosorb W) at a temperature of 100° showed four peaks and each was collected.

The first peak (581 mg, 72.2%) was identified as a mixture of **1** (36%) and its *exo* epimer (64%) by comparison of the ir and nmr spectra and gc retention times with those of authentic samples. The 36:64 ratio was assigned from integration of the nmr spectrum of the acetate mixture prior to reduction. It was found that this mixture of *exo*- and *endo*-[2.2.0] alcohols could not be separated by gc (a wide variety of columns and conditions were investigated), alumina column chromatography, or thin layer chromatography on silica gel.

The second peak (101 mg, 12.5%) was identified as *cis*-bicyclo[3.1.0]hexan-2-ol by comparison of its ir and nmr spectra and gc retention time with those of an authentic sample. The third (5.2%) fourth (10.1%) peaks were collected and spectrally shown to be alcohols, but no positive identification was made.

cis-**Bicyclo[3.1.0]hexan-2-ol.**—The method of Corey and Dawson[18] was followed to prepare this compound from 15.8 g (0.188 mol) of 2-cyclopentenol, 84.8 g (0.316 mol) of methylene iodide, and 30.7 g (0.474 mol) of zinc–copper couple.[18] The product was distilled through a 30-cm Vigreux column to give 11.66 g (63% yield), bp 58–48° (7–4 mm), $n^{28.5}\text{D}$ 1.4782[28] [lit.[18] 60% yield, bp 60–61° (10 mm)]. Gc analysis on a β,β'-oxydipropionitrile column showed the product to be formed in >87% yield contaminated with 3-cyclohexenol. The integrated nmr spectrum of the mixture indicated only 6% 3-cyclohexenol to be present and is believed to be correct owing to the overlap of the gc peaks.

cis-**Bicyclo[3.1.0]hex-2-yl Acetate (10).**—This acetate was prepared by the reported procedure.[20] The product obtained in 94% yield was analyzed on a newly prepared Carbowax 20M gc column (20% on Chromosorb W) and found to give partial separation of acetates **10** (94%) and **11** (6%) under analytical conditions. The integrated nmr spectrum agreed with this analysis and supports the nmr spectral analysis of the starting alcohol mixture.

Bicyclo[3.1.0]hexan-2-one.—A solution of 13.5 g (0.133 mol) of chromic anhydride in 20 ml of distilled water was added, with cooling, over a period of 20 min to 5.0 g (51 mmol) of the mixture containing *cis*-bicyclo[3.1.0]hexan-2-ol (prepared above) in 20 ml of ether. The resulting mixture was stirred at room temperature for 4 hr and worked up by separating the layers and extracting the aqueous layer with two 20-ml portions of ether. The ether fractions were washed with three 15-ml portions of saturated sodium bicarbonate solution and two 20-ml portions of saturated sodium chloride solution, dried, concentrated at reduced pressure, and trap-to-trap distilled [27° (0.05 mm)]. The light yellow liquid (2.44 g, 50% yield) was analyzed by gc on a Carbowax 20M column and showed a single major peak. The ir and nmr spectra were in excellent agreement with the assigned structure. A 2,4-dinitrophenylhydrazone of this ketone was prepared and recrystallized from aqueous ethanol, mp 188.5–189.5°.

Anal. Calcd for $C_{12}H_{12}N_4O_4$: C, 52.17; H, 4.38. Found: C, 52.35; H, 4.48.

trans-**Bicyclo[3.1.0]hexan-2-ol.**—Bicyclo[3.1.0]hexan-2-one (2.4 g, 25.0 mmol), prepared as described above, was reduced with 14.8 g (72.5 mmol) of freshly sublimed aluminum isopropoxide in 74 ml of dry isopropyl alcohol by stirring under reflux for 18 hr. The reaction mixture was cooled to room temperature, 100 ml of water added, the mixture was neutralized with concentrated hydrochloric acid and extracted with five 30-ml portions of pentane. The pentane solution was washed with 40 ml of saturated sodium chloride solution, dried, concentrated, and trap-to-trap distilled [50° (0.005 mm)]. The light yellow liquid product (1.3 g, 53% yield) was analyzed by gc on a β,β'-oxydipropionitrile column and three peaks were observed in a 33:48:19 ratio. The first peak was identified as starting ketone, and the second and third peaks were identified as *trans*- and *cis*-bicyclo[3.1.0]hexan-2-ols, respectively. The ir and nmr spectra of the collected second gc peak agreed with those previously reported.[20]

trans-**Bicyclo[3.1.0]hex-2-yl Acetate.**—This compound was prepared by the method previously reported[20] in 65% yield from crude *trans* alcohol. The nmr spectrum showed the presence of a trace of 3-cyclohexenyl acetate and 12% *cis*-bicyclo[3.1.0]hex-2-yl acetate.

Registry No.—**3**, 19203-09-9; **4**, 19203-58-8; **6**, 19203-10-2; **7**, 19203-11-3; **8**, 19203-12-4; **12**, 19203-13-5; 2,4-dinitrophenylhydrazone of bicyclo-[3.1.0]hexan-2-one, 19203-59-9; bicyclo[2.2.0]hex-2-yl methylsulfinylmethyl ketone, 19245-02-4.

Acknowledgment.—The authors wish to express their gratitude to the National Science Foundation (GP-4888, GP-7818) for support of this research and for a departmental grant for the purchase of the Varian A-60 nmr spectrometer.

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[28] W. G. Dauben and G. H. Berezin [*J. Amer. Chem. Soc.*, **85**, 468 (1963)] have reported the refractive index to be $n^{25}\text{D}$ 1.4742.