Additional attempts to reduce (XX) with lithium aluminum hydride were made, but in each case products were formed which quickly decomposed to highly colored materials which decomposed further. No attempt was made to characterize these products.

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6-Substituted Bicyclo[3.1.1]heptanes[1]

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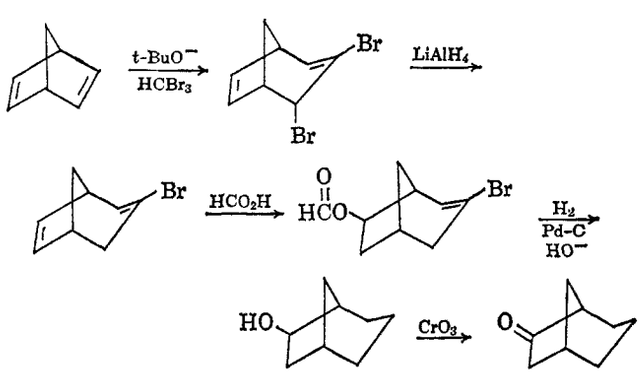
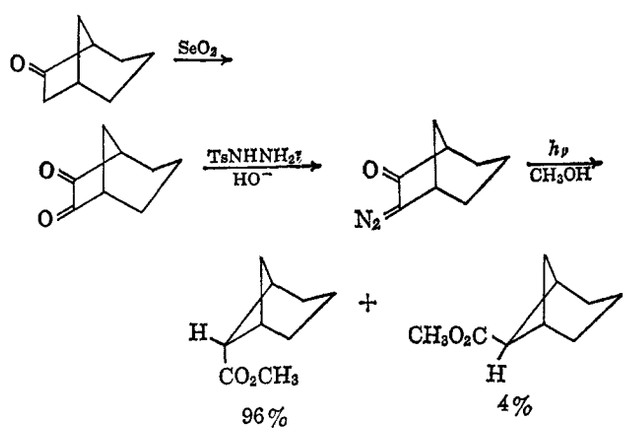
The synthesis of some 6-substituted bicyclo[3.1.1]heptanes is described, and the nmr spectra are discussed and compared with those of the corresponding bicyclo[2.1.1]hexanes.

In connection with another study, several 6-substituted bicyclo[3.1.1]heptanes were needed. The simplest method for obtaining these compounds would be *via* the ring contraction of bicyclo[3.2.1]octan-6-one, in analogy with the preparation of 5-substituted bicyclo[2.1.1]hexanes from norcamphor and its derivatives.[3] The preparation of 3-bromobicyclo[3.2.1]oct-3-en-6-yl formate was effected by the procedure of Sauers[4] in which dibromocarbene is added to norbornadiene,[5] followed by lithium aluminum hydride reduction and addition of formic acid. Hydrogenation using palladium on carbon in basic solution led to reduction of the double bond, hydrogenolysis of the bromine, and hydrolysis of the formate group, leading to bicyclo[3.2.1]octan-6-ol. Oxidation with chromic acid gave the ketone.



Selenium dioxide converted the ketone to bicyclo[3.2.1]octa-6,7-dione (76%) which was converted to the monotosylhydrazone (75%) and then to 7-diazobicyclo[3.2.1]octan-6-one (83%) with aqueous base. Photolysis of the diazo ketone in anhydrous methanol gave methyl bicyclo[3.1.1]heptane-6-carboxylate (75%). Vapor phase chromatography indicated the presence of two compounds in a 96:4 ratio.

The major fraction from the photolysis was shown to be the *endo* isomer by its nmr spectrum. It had a



doublet at τ 8.76 (J = 9.0 cps) which corresponds to the upfield doublet of the 5-*endo*-substituted bicyclo[2.1.1]hexanes.[3,6] The proton is presumably the *endo* hydrogen on the methylene bridge, and the coupling constant is that for the *gem* coupling. The minor fraction appeared to be the *exo* isomer, because of the identity of its retention time with that of an authentic sample of the *exo* ester prepared as described below. The *exo* isomer could be identified by its nmr spectrum. It had a multiplet at τ 8.71 corresponding to two doublets (J = 9.0 and 6.0 cps). The 9.0-cps coupling constant results from the *gem* coupling, and the 6.0-cps constant results from the long-range coupling between the *endo* protons on the four-membered ring. This is again analogous to the bicyclo[2.1.1]hexanes.[3,6] Throughout the series of compounds to be discussed, the configuration could be established by an examination of the upfield band. The nmr spectra of all of the compounds will be discussed at the end of this paper.

The pure *endo* methyl ester was isolated by preparative vpc. Reduction with lithium aluminum hydride gave *endo*-bicyclo[3.1.1]heptane-6-carbinol.

endo-Bicyclo[3.1.1]heptane-6-carboxylic acid was prepared by base-catalyzed hydrolysis of the ester. It was converted to the acid chloride with thionyl chloride, and still had the *endo* configuration as shown by the nmr spectrum. The acid chloride was treated with the magnesium salt of diethyl malonate, and the product was subjected to acid hydrolysis giving bicyclo[3.1.1]heptyl-6 methyl ketone. The upfield nmr band was a multiplet, suggesting that epimerization had

(1) This work was supported by the Army Research Office (Durham).

(2) Taken from part of the Ph.D. thesis of B.A.H., 1966.

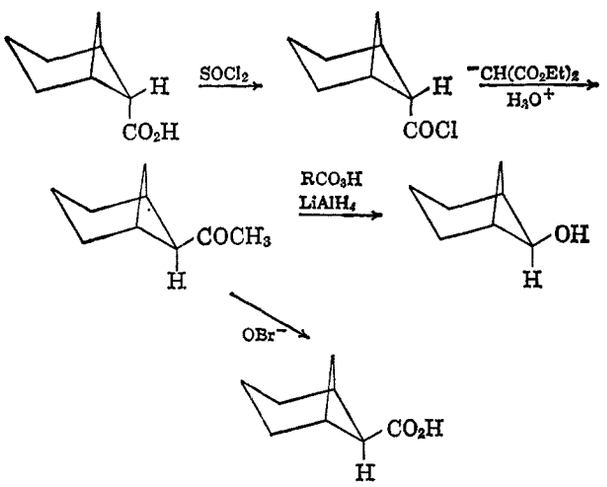
(3) L. Horner and E. Spietschka, *Ber.* **88**, 934 (1955); J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 2857 (1960); **82**, 5445 (1960); K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3998 (1961); K. B. Wiberg and B. R. Lowry, *ibid.*, **85**, 3188 (1963); J. Meinwald, C. B. Jensen, A. Lewis, and C. Swithenbank, *J. Org. Chem.*, **29**, 3469 (1964).

(4) R. R. Sauers and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964). We thank Professor Sauers for supplying the detailed procedure prior to publication.

(5) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

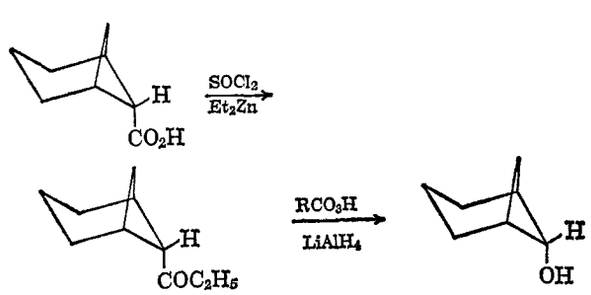
(6) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962).

occurred. Treatment of the ketone with *m*-chloroperbenzoic acid gave bicyclo[3.1.1]heptyl-6 acetate. The nmr spectrum of the acetate had a triplet at τ 5.32 and a doublet at τ 5.69. These bands result from the proton attached to the carbon bearing the acetate group in the two isomers. The first must have the proton in the *exo* position in order to couple with the two bridgehead protons and give a triplet, whereas the second must have the proton in the *endo* position in order to give a doublet *via* the long-range coupling. From the intensity of the bands, the *exo*:*endo* ratio was 80:20. It was not possible to separate the isomers by vpc. The epimerization observed here is analogous to the results of Meinwald and Gassman with some bicyclo[2.1.1]hexane derivatives.[3]



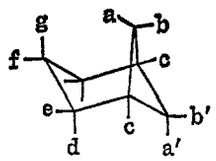
Lithium aluminum hydride reduction of the mixture of acetates gave bicyclo[3.1.1]heptan-6-ol, with an 80:20 *exo*:*endo* ratio. It was again not possible to separate the isomers by vpc.

It was possible to obtain mainly the *endo* ethyl ketone *via* the reaction of the acid chloride with diethylzinc. This is a very convenient reaction, and appears to be superior to the use of dialkylcadmium, especially since the diethylzinc may readily be obtained in pure form. The ketone was treated with *m*-chloroperbenzoic acid to give *endo*-bicyclo[3.1.1]heptyl- 6 propionate, contaminated with about 20% of the *exo* isomer. Lithium aluminum hydride reduction gave the *endo* alcohol, again containing about 20% of the *exo* isomer.



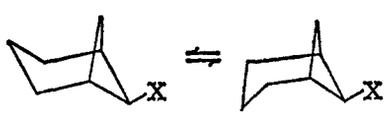
Since the *exo* methyl ketone had been obtained *via* the reactions used, it was possible conveniently to obtain *exo*-bicyclo[3.1.1]heptane-6-carboxylic acid by hypobromite oxidation. The acid was converted to the methyl ester. The mixture of methyl esters (80% *exo* and 20% *endo*) was separated by preparative vpc and the pure *exo* ester was reduced to *exo*-bicyclo[3.1.1]heptane-6-methanol by lithium aluminum hydride.

The availability of these compounds permits an interesting comparison of the nmr spectra with those of the corresponding bicyclo[2.1.1]hexanes.[6] The spectra of the compounds obtained in the present work are summarized in Table I. The several types of protons are designated as shown below and the substituent will replace either a′ or b′.



The more obvious differences in going from the bicyclo[2.1.1]hexanes to the bicyclo[3.1.1]heptanes are the following: (1) the *gem* coupling constant, J_{ab}, increased from 6.5–7.5 cps to 8.5–9.5 cps; (2) the long-range coupling constant, $J_{aa'}$, decreased from 7–8 cps to 5.5–6.0 cps; (3) the coupling constant to the bridgehead protons, J_{bc}, increased from 2.7–3.3 cps to 6.0 cps; and (4) a downfield shift of about 0.3–0.4 ppm for the a and b protons. The decrease in long-range coupling probably indicates that the cyclobutane ring is less puckered in the bicycloheptanes than in the bicyclohexanes, since the coupling constant appears to be correlated with the distance between the carbons involved.[7] The small value of J_{bc} found with the bicyclohexanes suggested that the dihedral angle between the b and c protons may be on the order of 40–50°; the considerable increase observed with the bicycloheptanes indicates that the angle has decreased, perhaps to a value on the order of 20–30°. The change in the *gem* coupling constant indicates that the *gem* bond angle has also changed. It is clear that the increase in the size of the ring attached across the cyclobutane ring has resulted in a considerable decrease in the nonplanarity of the latter ring.

It may also be noted that the protons designated as d, e, f, and g appear as a fairly sharp singlet in the *exo*-bicyclo[3.1.1]heptane derivatives. This probably results, at least in part, from a rapid conformational flip similar to that found with cyclohexane (see below).



With most of the *endo* derivatives, on the other hand, the signals due to these protons gave a broad multiplet suggesting that the ring may have been forced into one of the two conformations in order to minimize nonbonded repulsive interactions. The temperature dependence of the nmr spectra of these compounds is under study in order to determine the barrier to the conformational inversion.

Experimental Section

3-Bromobicyclo[3.2.1]oct-2-en-6-yl Formate.[4]—A 15% solution (by weight) of 152 g (0.82 mole) of 3-bromobicyclo[3.2.1]-

(7) *Cf.* the data presented by K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

TABLE I

THE NMR SPECTRA OF 6-BICYCLO[3.1.1]HEPTANE DERIVATIVES[a]

Compd	a	b′(a′)	c	d, e, f, g	Other (J, cps)	J_{ab}, cps	J_{bc}, cps	$J_{aa'}$, cps
endo-6-								
$COOCH_3$	8.76 (d)	7.18 (t)	7.42 (t)	~8.2 (b)	CH_3 6.40 (s)	9.0	6.0	
COOH	8.75 (d)	7.09 (t)	7.38 (t)	~8.1 (b)	COO*H* −2.15 (s)	9.0	6.0	
COCl	8.70 (d)	6.70 (t)	7.21 (t)	~8.1 (b)		9.5	6.0	
$COCH_2CH_3$	8.86 (d)	...	...	~8.1 (b)	CH_2CH_3 7.70 (q) (7.0) CH_3 9.00 (t) (7.0)	9.0	[b]	
$OCOCH_2CH_3$	...	5.31 (t)	7.45 (m)	~8.15 (b)	CH_2CH_3 7.71 (q) (7.5) CH_3 8.88 (t) (7.5)	[b]	6.0	
OH	...	6.00 (t)	7.66 (m)	~8.15 (b)	O*H* 5.78 (s)	[b]	6.0	
OTs	8.52	5.43 (t)	7.55[c]	8.28 (m)	C_6H_4 2.20, 2.66 CH_3 7.56 (s)	[b]	[b]	
CH_2OH	8.51 (d)	...	7.69 (m)	8.27 (m)	CH_2OH 6.43 (d) (7.5) O*H* 5.59 (s)	9.5	[b]	
CH_2OTs	8.55 (d)	...	7.65 (b)[c]	8.33 (m)	C_6H_4 2.28, 2.72 CH_3 7.57 (s) CH_2 6.00 (d) (7.0)	9.5	[b]	
exo-6-								
$COCH_3$	8.75 (m)	7.52 (d)	7.48	8.12 (s)	$COCH_3$ 7.92 (s)	9.0	[b]	5.5
$OCOCH_3$	8.5 (m)	5.69 (d)	7.69	...	$OCOCH_3$ 8.01 (s)	[b]	[b]	6.0
OH	8.53 (m)	6.32 (d)	...	...	O*H* 5.60 (s)	8.5	[b]	6.0
OTs	...	5.76 (d)	7.6[c]	...	C_6H_4 2.29, 2.72 CH_3 7.55 (s)	[b]	[b]	6.0
COOH	8.7 (m)	7.60 (d)	7.40	8.11 (s)	COO*H* −2.37 (s)	8.5	[b]	6.0
$COOCH_3$	8.71 (m)	7.70 (d)	7.45	8.11 (s)	CH_3 6.36 (s)	9.0	[b]	6.0
CH_2OH	8.68 (m)	...	7.90	8.18 (s)	CH_2OH 6.32 (d) (7.5) O*H* 5.80 (s)	9.0	[b]	5.5
CH_2OTs	8.68 (m)	...	7.93	8.21 (s)	CH_2 5.86 (d) (8.0) C_6H_4 2.29, 2.72 CH_3 7.57 (s)	[b]	[b]	[b]

[a] The abbreviations are s, singlet; d, doublet; t, triplet; q, quartet; m, partially resolved multiplet; b, broad. The bands due to the b protons could not be located in any derivatives. [b] The spectrum was not well enough resolved that an assignment could be made. [c] The peak position is uncertain since it is very close to a more intense band.

octadiene[6] in formic acid (98–100%) was stirred at room temperature for 3 days. The solution was diluted with three times its volume of water and neutralized with solid sodium bicarbonate. The mixture was extracted three times with 1-l. portions of ether. After drying, distillation gave 169 g (90%) of the bromo formate, bp 90–105° (0.05–0.1 mm).

Bicyclo[3.2.1]octan-6-ol.—A mixture of 40 g (0.175 mole) of 3-bromobicyclo[3.2.1]oct-2-en-6-yl formate, 160 ml of tetrahydrofuran, 212 ml of 2 *N* sodium hydroxide solution, and 10 g of 5% palladium on charcoal was treated with hydrogen using a Parr apparatus until no more hydrogen was taken up (approximately 4 hr). The solution was filtered and the filtrate was diluted with 900 ml of water and acidified with 1 *N* hydrochloric acid. The mixture was extracted with three 300-ml portions of ether. After drying, distillation of the solvent gave 19.7 g (90%) of a brown solid which could be used without further purification. A small amount of the alcohol was sublimed and further purified by vpc and then had mp 144–145° (lit.[8] mp 147–149°).

Bicyclo[3.2.1]octan-6-one.—To a stirred solution of 78.5 g (0.62 mole) of crude bicyclo[3.2.1]octan-6-ol in 290 ml of acetone was added dropwise a solution of 103 g (0.97 mole) of chromium trioxide and 84 ml of concentrated sulfuric acid diluted to a total volume of 380 ml with water. The temperature was kept between 20 and 30° using an ice–water bath. The chromic acid solution was added until the orange-brown color persisted. The mixture was allowed to stand overnight at room temperature. Sodium bisulfite was then added until the green color persisted. The liquid was decanted from the green sludge, and the latter was washed three times with acetone. The combined acetone solution was washed three times with saturated potassium carbonate solution. After drying over anhydrous potassium carbonate, the acetone was removed by distillation and the residue was sublimed giving 69.5 g (90%) of the ketone, mp 137–141°. A small amount of the ketone was further purified by vpc and then had mp 155–157° (lit.[7] mp 157–159°.)

(8) G. Komppa, T. Hirn, W. Rohrmann, and S. Beckman, *Ann.*, **521**, 242 (1936).

Bicyclo[3.2.1]octa-6,7-dione.—To a solution of 65 g (0.52 moles) of bicyclo[3.2.1]octan-6-one in 85 ml of xylene was added 61.5 g (0.56 moles) of freshly sublimed selenium dioxide. The mixture was vigorously stirred and heated to reflux for 4 hr. It was cooled and filtered, and the precipitate was washed with benzene. The benzene solution was added to the reaction mixture, and the solvent was removed using a rotary evaporator with a 90° bath temperature. Distillation of the residue gave 55 g (76%) of an orange solid, bp 130–170° (0.1–0.5 mm). The crude product was immediately used in the next reaction.

Bicyclo[3.2.1]octa-6,7-dione Monotosylhydrazone.—To a solution of 164 g (1.2 mole) of bicyclo[3.2.1]octa-6,7-dione in 157 ml of acetic acid cooled in an ice–water bath was added in portions a boiling solution of 222 g (1.2 mole) of *p*-toluenesulfonylhydrazide in 342 ml of acetic acid. The product begins to precipitate when about half of the latter solution is added. The mixture was kept in a refrigerator overnight. It was filtered by suction and the solid washed generously with water. The wet yellow solid was dried under reduced pressure over phosphorus pentoxide to give 277 g (76%) of the tosylhydrazone, mp 159–161° dec. A small portion was recrystallized three times from acetonitrile and had mp 160–161° dec.

Anal. Calcd for $C_{15}H_{18}N_2O_3S$: C, 58.8; H, 5.9; S, 10.5; N, 9.1. Found: C, 58.6, 58.8; H, 5.7, 5.8; S, 10.6, 10.7; N, 9.1, 9.1.

7-Diazobicyclo[3.2.1]octan-6-one.—To a stirred solution of 200 g (0.65 mole) of bicyclo[3.2.1]octa-6,7-dione monotosylhydrazone and 31.7 g (0.79 mole) of sodium hydroxide in 1500 ml of water was added 1700 ml of pentane. As the pentane became yellow, it was decanted and replaced by fresh pentane using a total of 17 l of pentane. The final portion was decanted after 12 hr. The pentane solution was dried and the solvent was removed by distillation to give 81.5 g (83%) of the crude diazo ketone. It was used in the following step without further purification.

Methyl *endo*-Bicyclo[3.1.1]heptane-6-carboxylate.—A solution of 81 g (0.53 mole) of crude 7-diazobicyclo[3.2.1]octan-6-one in 4500 ml of anhydrous methanol was irradiated with a water-cooled 450-w Hanovia immersion quartz lamp using a Corex

filter. It was irradiated for 8 hr after nitrogen evolution was no longer apparent (a total of about 36 hr). About 4 l. of the solvent was removed by distillation through a 30-in. Heli-Pak column. To the residue was added 1 l. of chopped ice and water; the mixture was extracted with four 1-l. portions of pentane. After drying, the pentane was removed by distillation through the column. Distillation of the residue gave 62.2 g (75%) of ester, bp 73–75° (8–9 mm). Analysis by vpc using a 5 ft × 3/4 in. didecyl phthalate column at 150° indicated two components: 96% of methyl *endo*-bicyclo[3.1.1]heptane-6-carboxylate (retention time 25 min) and 4% of another compound, later identified as methyl *exo*-bicyclo[3.1.1]heptane-6-carboxylate (see below) (retention time 28 min).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.1; H, 9.2. Found: C, 70.1, 70.1; H, 9.1, 9.0.

***endo*-Bicyclo[3.1.1]heptane-6-methanol.**—To a slurry of 1.0 g (26 mmoles) of lithium aluminum hydride in 100 ml of anhydrous ether was added a solution of 4.2 g (27 mmoles) of methyl *endo*-bicyclo[3.1.1]heptane-6-carboxylate in 50 ml of anhydrous ether. After the addition, the mixture was heated at reflux for 30 min. It was cooled in an ice bath and water was added with stirring until the solid settled in a slurry at the bottom of the flask when the stirrer was stopped. The ether solution was decanted and the aqueous phase was washed several times with ether. The combined ether solution was dried and distilled to give 3.3 g (96%) of the crude alcohol. It was purified by vpc using a 10 ft × 3/8 in. Carbowax column with 85% recovery.

Anal. Calcd for $C_7H_{14}O$: C, 76.1; H, 11.2. Found: C, 75.8, 75.8; H, 11.0,11.1.

***endo*-Bicyclo[3.1.1]heptane-6-methyl Tosylate.**—To a solution of 3.3 g (26 mmoles) of *endo*-bicyclo[3.1.1]heptane-6-methanol in 30 ml of dry pyridine cooled to 0° was added 5.6 g (30 mmoles) of *p*-toluenesulfonyl chloride. After the material had dissolved, the solution was placed in a refrigerator overnight. To the mixture was added 20 g of ice and 30 ml of water. It was extracted with three 100-ml portions of ether. The combined ether extract was washed with three 250-ml portions of 1 *N* sulfuric acid, once with 250 ml of water, and twice with 250-ml portions of saturated sodium bicarbonate solution. After drying, the solvent was removed by distillation to give 7.2 g of a crude white solid. It was recrystallized from pentane two times to give 6.2 g (84%) of pure tosylate, mp 57.8–58.4°.

Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.3; H, 7.2; S, 11.5. Found: C, 63.9, 64.0; H, 7.3, 7.1; S, 11.7, 11.5.

***endo*-Bicyclo[3.1.1]heptane-6-carboxylic Acid.**—A solution of 10.0 g (65 mmoles) of methyl *endo*-bicyclo[3.1.1]heptane-6-carboxylate and 7.3 g of potassium hydroxide in 43 ml of methanol was heated to reflux for 2.3 hr. About 15 ml of methanol was removed by distillation. The residue was cooled and diluted with 75 ml of ice–water mixture. The mixture was washed with three 75-ml portions of pentane. The aqueous solution was then acidified with concentrated hydrochloric acid and extracted with four 100-ml portions of pentane. After drying, the pentane was distilled through a 30-in. Heli-Pak column, and the residue was sublimed giving 8.6 g (95%) of the acid, mp 68–77°. A small portion was recrystallized twice from pentane and had mp 95.4–97.4°.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.7, 68.8; H, 8.3, 8.5.

***endo*-Bicyclo[3.1.1]heptane-6-carbonyl Chloride.**—A solution of 8.6 g (61 mmoles) of *endo*-bicyclo[3.1.1]heptane-6-carboxylic acid in 14.9 g (126 mmoles) of thionyl chloride was allowed to stand at room temperature for 1 hr and then heated on a steam bath for 4 hr. Distillation gave 8.8 g (91%) of the acid chloride, bp 71–72° (8–9 mm).

***exo*-6-Bicyclo[3.1.1]heptyl Methyl Ketone.**—Into a flask fitted with a mechanical stirrer, condenser, drying tube, and addition funnel was added 1.5 g (62 g-atoms) of magnesium turnings, 1.5 ml of absolute ethanol, and 0.14 ml of carbon tetrachloride. After the exothermic reaction had proceeded for several minutes, 42 ml of anhydrous ether was added cautiously to the mixture. A solution containing 9.78 g (61 mmoles) of freshly distilled diethyl malonate, 5.5 ml of absolute ethanol, and 7 ml of ether was added with stirring. The mixture was heated periodically during the addition to maintain reflux. After the addition was completed, the solution was heated for 3 hr at reflux. With vigorous stirring, a solution of 8.8 g (55 mmoles) of *endo*-bicyclo-[3.1.1]heptane-6-carbonyl chloride in 14 ml of anhydrous ether was added dropwise to the mixture over a period of 15 min. After heating for an additional 30 min, the mixture was cooled to 0° and a solution of 7 g of concentrated sulfuric acid in 55 ml of water was added dropwise with vigorous stirring. When the white solid had dissolved, the two phases were separated and the aqueous phase was extracted with 30 ml of ether. The combined ether solution was washed once with water, and the solvent was removed using a rotary evaporator. To the residue was added 16.7 ml of acetic acid, 2.1 ml of concentrated sulfuric acid, and 11 ml of water. The mixture was heated to reflux for 6 hr. The solution was cooled to 0° and made alkaline with 20% sodium hydroxide solution. Extraction with ether followed by drying and distillation of the ether solution gave 6.5 g (85%) of the methyl ketone, bp 73–75° (9–10 mm). The nmr spectrum indicated the material to be predominantly the *exo* isomer (~80%) along with some of the *endo* isomer. Separation by vpc was unsuccessful.

Anal. Calcd for $C_9H_{14}O$: C, 78.2; H, 10.2. Found: C, 77.9, 77.8; H, 10.0, 10.2.

***exo*-Bicyclo[3.1.1]heptane-6 Acetate.**—To a solution of 11.2 g of *m*-chloroperbenzoic acid (assay 85%) in 110 ml of methylene chloride was added 6.5 g (47 mmoles) of *exo*-6-bicyclo[3.1.1]-heptyl methyl ketone. The solution was allowed to stand for 12 days at room temperature, after which time 97–98% reaction had occurred. The mixture was extracted with three 28-ml portions of cold 10% sodium hydroxide solution, and then washed with 85 ml of water in two portions, 25 ml of 10% sodium bisulfite solution, and 25 ml of water. It was dried and distilled, giving 6.0 g (83%) of the acetate, bp 68° (9 mm). The nmr spectrum indicated a 4:1 *exo*:*endo* ratio.

Anal. Calcd for $C_9H_{12}O_2$: C, 70.1; H, 9.2. Found: C, 69.8, 70.0; H, 9.0, 9.1

***exo*-Bicyclo[3.1.1]heptane-6-carboxylic Acid.**—To a solution of 11.2 g (0.2 moles) of potassium hydroxide in 44 ml of water cooled to 3° was added 10.6 g (0.066 mole) of bromine with good stirring, maintaining the temperature between 3 and 7°. The solution was added dropwise to a solution of 3.0 g (22 mmoles) of *exo*-6-bicyclo[3.1.1]heptyl methyl ketone in 95 ml of dioxane. The mixture was stirred for 1 hr at room temperature and then heated at reflux for 30 min. After cooling to 0°, 22 ml of 8% potassium hydroxide solution was added. The mixture was extracted with three 400-ml portions of ether. Sodium bisulfite (0.8 g) was added to the aqueous solution and concentrated hydrochloric acid was added to make it acidic. The product was extracted with ether, and the ether solution was washed with water. Drying and distillation of the solvent gave 2.5 g (89%) of the acid. After sublimation it had a melting point of 52–55°.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.4, 68.4; H, 8.5, 8.5.

Methyl *exo*-Bicyclo[3.1.1]heptane-6-carboxylate.—The *exo*-bicyclo[3.1.1]heptane-6-carboxylic acid obtained above was converted to the methyl ester with diazomethane in ether. The crude ester was purified by preparative vpc using a 10 ft × 3/8 in diethylene glycol succinate column at 158°. The major isomer (*exo*, 84%) had a retention time of 33 min, and the minor isomer (*endo*, 16%) had a retention time of 29 min. From 6.0 g of the crude ester was obtained 3.2 g of the pure *exo* isomer.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.1; H, 9.2. Found: C, 70.4, 70.5; H, 9.2, 9.0.

***exo*-Bicyclo[3.1.1]heptane-6-methanol.**—A solution of 3.1 g (20 mmoles) of methyl *exo*-bicyclo[3.1.1]heptane-6-carboxylate in 50 ml of anhydrous ether was added to a slurry of 0.75 g (20 mmoles) of lithium aluminum hydride in 75 ml of anhydrous ether. After the addition was completed, the mixture was heated to reflux and stirred for 30 min. It was hydrolyzed with water and the ether phase was decanted from the aqueous solution. The latter was extracted with two portions of ether. The combined ether solution was dried and the solvent was removed by distillation giving 2.5 g (98%) of the alcohol. Analysis by vpc indicated it to be 99% pure.

Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 75.8, 75.8; H, 11.0, 11.1.

***exo*-Bicyclo[3.1.1]heptane-6-methyl Tosylate.**—A solution of 2.4 g (19 mmoles) of *exo*-bicyclo[3.1.1]heptane-6-methanol in 22 ml of pyridine was cooled in an ice–salt bath and 4.1 g (22 mmoles) of *p*-toluenesulfonyl chloride was added. The flask was stoppered, cooled, and swirled until all of the chloride had dissolved. It was then placed in a refrigerator. After 13 hr, 15 g of ice and 25 ml of water was added. The mixture was extracted with three 75-ml portions of ether. The ether solution was washed twice with 1 *N* sulfuric acid, twice with water, and once with saturated sodium bicarbonate solution. After drying,

distillation of the ether gave 4.8 g of the crude tosylate. It was recrystallized twice from pentane to give 3.6 g (68%) of white crystals, mp 44.6–44.8°.

Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.3; H, 7.2; S, 11.5. Found: C, 64.2, 64.4; H, 7.3, 7.1; S, 11.3, 11.6.

***exo*-Bicyclo[3.1.1]heptan-6-ol.**—A solution of 2.0 g (13 mmoles) of *exo*-bicyclo[3.1.1]heptane-6-acetate in 25 ml of anhydrous ether was added to a slurry of 0.38 g (10 mmoles) of lithium aluminum hydride in 50 ml of anhydrous ether with stirring over a period of 20 min. The mixture was heated at reflux and stirred for another 30 min. It was hydrolyzed with water, and the ether layer was separated. The aqueous layer was extracted twice with ether. The combined ether solution was dried, and the solvent was removed giving 1.5 g of crude alcohol. Analysis by vpc showed only one product other than solvent. Sublimation gave 1.3 g (90%) of a white solid, mp 72–78°. The broad melting range is presumably due to the small amount of the *endo* isomer which was present. All attempts to separate the epimers by vpc were unsuccessful.

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 75.2, 75.3; H, 10.7, 10.9.

***exo*-Bicyclo[3.1.1]heptane-6 Tosylate.**—A solution of 6.9 g (61 mmoles) of *exo*-bicyclo[3.1.1]heptan-6-ol in 69 ml of dry pyridine was cooled in an ice–salt bath and 13 g (69 mmoles) of *p*-toluenesulfonyl chloride was added. After 12 hr in a refrigerator, the crude tosylate was isolated as described for the other tosylate above. In order to remove the small amount of the more reactive *endo* isomer which was present, the crude tosylate was added to 500 ml of anhydrous acetic acid and 4 g of sodium carbonate. The solution was allowed to stand at room temperature for 70 min. The mixture was diluted with 800 ml of water and extracted with three 300-ml portions of pentane. The pentane solution was washed with two 500-ml portions of water, 500 ml of 2.5% sodium bicarbonate solution, and 500 ml of water. After drying, the pentane was removed by distillation. The residue was heated for 1 hr at 45° and 0.1-mm pressure. The residue was recrystallized from pentane–ether giving 10.2 g of a slightly yellow solid. It was heated at 45° (0.05 mm) for 6 hr and recrystallized from pentane–ether to give 9.2 g (57%) of the tosylate, mp 63.8–64.5°.

Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.1; H, 6.8; S, 12.0. Found: C, 63.4, 63.2; H, 6.8, 6.8; S, 11.9, 12.0.

***endo*-6-Bicyclo[3.1.1]heptyl Ethyl Ketone.**—Diethylzinc (Columbia Organic Chemicals, 2.8 g, 22.6 mmoles) was added to 75 ml of anhydrous ether under nitrogen. To the stirred solution was added dropwise 6.0 g (38 mmoles) of *endo*-bicyclo[3.1.1]-heptane-6-carbonyl chloride. After the addition was completed, the mixture was heated to reflux for 3 min. The heat was removed and the mixture continued to reflux for approximately 12 min. The solution was then heated for an additional 3 min. A saturated solution of ammonium chloride (50 ml) was added *cautiously*. The aqueous layer was separated and washed with ether. The combined ether solution was washed with saturated sodium bicarbonate solution and with water. The ether was removed using a rotary evaporator giving 5.3 g (92%) of the crude ketone which was used directly in the following procedure.

***endo*-Bicyclo[3.1.1]heptane-6 Propionate.**—Crude *endo*-6-bicyclo[3.1.1]heptyl ethyl ketone (15.0 g, 99 mmoles) was added to a slurry of 40 g (0.2 mole) of *m*-chloroperbenzoic acid (85% assay) in 115 ml of methylene chloride and stirred for 3 days. The mixture was filtered, the filtrate was cooled to 0°, and cold 10% sodium hydroxide solution was added to give a pasty solid and liquid. Solid sodium bisulfite was added until the solid dissolved. The layers were separated. The organic layer was washed twice with 10% sodium hydroxide solution, once with 10% sodium bisulfite solution, and once with water. After drying, distillation gave 11.6 g (69%) of the ester, bp 100–102° (18–19°). The nmr spectrum indicated an *endo*:*exo* ratio of 4:1.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.2, 71.2; H, 9.7, 9.6.

***endo*-Bicyclo[3.1.1]heptan-6-ol.**—To a slurry of 1.0 g (26 mmoles) of lithium aluminum hydride in 50 ml of ether was added a solution of 5.3 g (32 mmoles) of *endo*-bicyclo[3.1.1]-heptane-6 propionate in 40 ml of anhydrous ether dropwise over a period of 20 min. The solution was heated to reflux for 30 min and then hydrolyzed with water. The ether layer was separated and the aqueous phase was washed twice with ether. The combined ether solution was dried and the ether was removed by distillation. The remaining solvent was removed by heating at 50° and 15 mm, giving 3.2 g of a soft solid. Analysis by vpc indicated that only one major product was present. Sublimation gave 2.9 g (82%) of a white solid, mp 107–124°. The broad melting range is probably due to the presence of the *exo* isomer (~20%) which could not be removed by vpc.

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.7. Found: C, 74.7, 74.8; H, 10.7, 10.6.

***endo*-Bicyclo[3.1.1]heptene-6 Tosylate.**—*endo*-Bicyclo[3.1.1]-heptan-6-ol (~20% *exo*, 1.2 g, 11 mmoles) in 40 ml of anhydrous ether was cooled to −5°. *p*-Toluenesulfonyl chloride (2.2 g, 11.5 mmoles) was added with stirring to attain solution. Small portions of powdered potassium hydroxide were added with stirring at 10-min intervals over a period of 1.75 hr. A total of 1.8 g of potassium hydroxide was used. The mixture was kept at −5° during this period. The mixture was placed in a freezer (−17°) overnight. To the mixture was added 80 g of ice and water. The ether layer was separated and the aqueous layer was extracted with two portions of ether. The combined ether solution was dried over anhydrous potassium carbonate. The ether was removed using a rotary evaporator with the flask immersed in water at room temperature. To the residual oil was added about 20 ml of pentane and enough ether to effect solution. The solution was evaporated using a rotary evaporator until about 5 ml of solvent was left and crystals were present. The mixture was cooled to −80° in Dry Ice and the solvent was decanted. This procedure was repeated giving 2 g (68%) of white tosylate. The compound could be stored without decomposition at Dry Ice temperature.