

from benzene; the Reissert compound stays in solution and can be precipitated by addition of petroleum ether solvent. Recrystallization from diisopropyl ether is effective, provided only a small amount of the acid is present. By combining these methods a sample of pure 2-*p*-chlorobenzoyl-1,2-dihydroisoquinaldonitrile (IVb) was obtained, m.p. 155.2–155.8°.

Anal. Calcd. for $C_{17}H_{11}N_2OCl$: C, 69.27; H, 3.76; N, 9.51; Cl, 12.03. Found: C, 69.30; H, 3.60; N, 9.50; Cl, 12.04.

Acid-catalyzed Cleavage of 2-*p*-Chlorobenzoyl-1,2-dihydroisoquinaldonitrile (IVb).—To a mixture of 1.00 g. (0.0034 mole) of 2-*p*-chlorobenzoyl-1,2-dihydroisoquinaldonitrile (IVb) and 0.67 g. (0.0032 mole) of 2,4-dinitrophenylhydrazine was added 20 cc. of concentrated hydrochloric acid. The mixture was heated on the steam-bath for half an hour, allowed to stand at room temperature for 48 hours, then diluted with water, heated to boiling, filtered and the precipitate washed with hot water and dried. After crystallization from nitrobenzene 0.80 g. (50%) of *p*-chlorobenzaldehyde 2,4-dinitrophenylhydrazone, m.p. 267–268°

(lit. m.p. 270°, 265°, 264°⁴³) was obtained. No attempt was made to isolate isoquinaldic acid.

Dimorphism of Reissert Compounds.—Some evidence for the occurrence of dimorphism in various Reissert compounds has accumulated in the course of our work. On several occasions a sample of 1-benzoyl-1,2-dihydroquinaldonitrile (Ia) of m.p. 142.5–143.5° was obtained. On standing it gradually changed over to the usual form of m.p. 154–155°. Also, on one occasion for each case, we have observed a m.p. of 96–99° for 1-benzoyl-6-methoxy-1,2-dihydroquinaldonitrile (Ib), the usual value being 127°, and a m.p. of 56–57° for 2-benzoyl-1,2-dihydroisoquinaldonitrile (IVa), the usual value being 125–126°. In both of these cases, too, the lower melting variety was readily transformed into the higher melting form. Dimorphic forms of methylphenyl-2-quinolylcarbinol (IIa) were also isolated in these studies.

(41) J. J. Blanksma and M. L. Wackers, *Rec. trav. chim.*, **55**, 659 (1936).

(42) J. Graymore and D. R. Davis, *J. Chem. Soc.*, 293 (1945).

(43) A. Eitel and G. Lock, *Monatsh.*, **72**, 385 (1939).

UPTON, LONG ISLAND, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

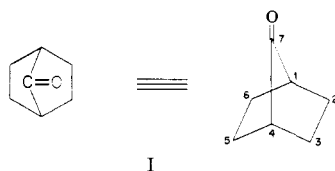
Studies in the Bicyclo[2.2.1]heptane Series.¹ III. Some Aliphatic Bicyclo[2.2.1]-7-heptanones²

BY PELHAM WILDER, JR., AND ANTHONY WINSTON³

RECEIVED AUGUST 15, 1955

Three derivatives of bicyclo[2.2.1]-7-heptanone are reported. *endo-cis*-Bicyclo[2.2.1]-7-heptanone-2,3-dicarboxylic acid (IV), *exo-cis*-2,3-dimethylbicyclo[2.2.1]-7-heptanone (V) and *endo-cis*-2,3-dimethylbicyclo[2.2.1]-7-heptanone (VI) were prepared from adducts of 6,6-dimethylfulvene and maleic anhydride. These carbonyl bridge compounds are stable toward heat, form carbonyl derivatives, and exhibit strong absorption bands near 5.63 μ in the infrared.

While many derivatives of bicyclo[2.2.1]-7-heptanone have been reported in the chemical literature, almost without exception they have been polyaryl or highly halogenated compounds and have contained an ethylenic double bond in the six-membered ring. In 1901, Zelinsky reported the preparation of the parent compound, bicyclo[2.2.1]-7-heptanone (I), by pyrolysis of the barium salt of *trans*-hexahydroterephthalic acid,⁴ but on repeating



Zelinsky's work Allen and his co-workers unequivocally demonstrated that Zelinsky had none of the ketone he reported.⁵ In 1893, in an attempt to prepare tetrachlorocyclopentadienone from hexachlorocyclopenten-3-one, Zincke and Günther obtained hexachloroindone and phosgene.⁶ In two later papers^{7,8} Zincke explained the results of the

(1) For paper II in this series, see P. Wilder, Jr., and A. Winston, *THIS JOURNAL*, **77**, 5598 (1955).

(2) Taken from a thesis submitted by Anthony Winston to the Graduate School of Duke University in partial fulfillment of the requirements for the Ph.D. degree, October, 1954.

(3) Du Pont Pre-doctoral Fellow, 1953–1954.

(4) N. Zelinsky, *Ber.*, **34**, 3798 (1901).

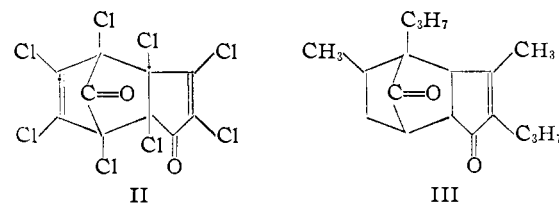
(5) C. F. H. Allen, T. Davis, D. W. Stewart and J. A. Van Allan, *J. Org. Chem.*, **20**, 306 (1955).

(6) T. Zincke and H. Günther, *Ann.*, **272**, 243 (1893).

(7) T. Zincke and K. H. Meyer, *ibid.*, **367**, 1 (1909).

(8) T. Zincke and W. Pfaffendorf, *ibid.*, **394**, 3 (1912).

previous investigation by suggesting that as soon as tetrachlorocyclopentadienone was formed, it dimerized to form II, perhaps the first synthetic bicyclo[2.2.1]-7-heptanone, which then readily lost carbon monoxide and chlorine to yield hexachloroindone. Polyaryl derivatives of bicyclo-



[2.2.1]-7-heptanone have been extensively investigated since 1933⁹ and very recently the preparation of some halogenated bicyclic ketones of this type has been reported by McBee and his collaborators.¹⁰ The only credible report of a bicyclo[2.2.1]-7-heptanone derivative with no phenyl groups or halogen atoms attached and with no double bond in the six-membered ring has been made by Allen and Van Allan¹¹ who prepared the tricyclic ketone III by catalytic hydrogenation of the dimer of allethrolone.¹² The purpose of the present paper

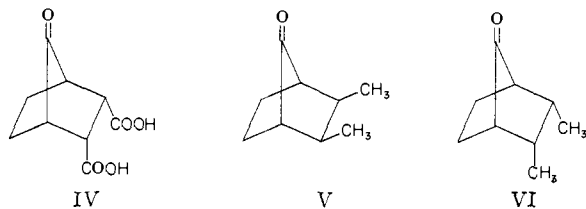
(9) C. F. H. Allen and E. W. Spanagel, *THIS JOURNAL*, **55**, 3773 (1933). For a review of the literature of carbonyl bridge compounds, see C. F. H. Allen, *Chem. Revs.*, **37**, 209 (1945).

(10) E. T. McBee, W. R. Diveley and J. E. Burch, *THIS JOURNAL*, **77**, 385 (1955).

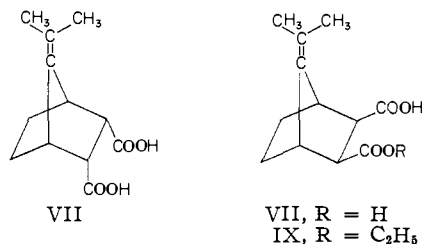
(11) C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, **20**, 323 (1955).

(12) F. B. La Forge, N. Greene and M. S. Schechter, *THIS JOURNAL*, **74**, 5392 (1952).

is to describe the preparation and properties of three aliphatic derivatives of the parent compound I: namely, *endo-cis*-bicyclo[2.2.1]-7-heptanone-2,3-dicarboxylic acid (IV), *exo-cis*-2,3-dimethylbicyclo[2.2.1]-7-heptanone (V) and *endo-cis*-2,3-dimethylbicyclo[2.2.1]-7-heptanone (VI).

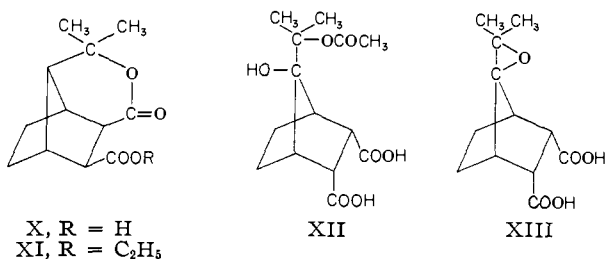


The original purpose of this investigation was the preparation of ketone I; but, due to circumstances which will be discussed in another publication, this goal was not realized. Instead, the conversion of readily available intermediates into derivatives of the parent compound was undertaken. The intermediates utilized were *endo-cis*-7-isopropylidenebicyclo[2.2.1]-heptane-2,3-dicarboxylic acid (VII) and its anhydride and the corre-



sponding *exo-cis*-isomer VIII and its anhydride. These were prepared from the respective addition products of 6,6-dimethylfulvene and maleic anhydride.^{1,13,14}

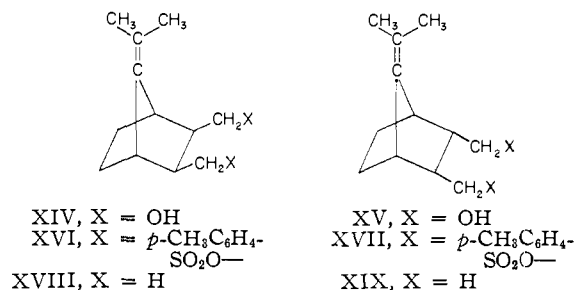
In experiments directed toward cleavage of the isopropylidene double bond, the anhydride of *endo-cis*-acid VII in the presence of peracetic acid was converted in fair yield into hydroxy acetate XII which in alkaline medium formed the epoxide XIII¹⁵; and peracetic acid oxidation of the anhydride of *exo-cis*-acid VIII and *exo*-acid ester IX under the same experimental conditions afforded hydroxy lactones X¹³ and XI¹, respectively. However, because of the relative stability of these intermediate oxidation products toward further oxidation, this route was abandoned in favor of a more nearly direct approach in the form of the ozonolysis reaction.



(13) K. Alder and R. Rühmann, *Ann.*, **566**, 1 (1950).
 (14) D. Craig, J. J. Shipman, J. Kiehl, F. Widmer, R. Fowler and A. Hawthorne, *THIS JOURNAL*, **76**, 4573 (1954).
 (15) The stereochemical assignment about carbon atom C7 in compounds XII and XIII is completely arbitrary.

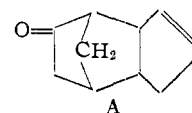
When the *exo*-acid ester IX was treated with ozone in ethyl acetate solution, there was isolated a viscous oil which could not be induced to crystallize; but a strong band at 5.61 μ in the infrared^{6,16} and the formation of a 2,4-dinitrophenylhydrazone strongly suggested that the oil contained at least some of a carbonyl bridge compound. In like manner the anhydride of *endo-cis*-acid VII gave an oil which yielded no pure compound, but did form a carbonyl derivative. In a further experiment the *endo-cis*-acid VII on treatment with ozone did yield a crystalline product which exhibited a strong band at 5.62 μ in the infrared and a low intensity band at 275 $m\mu$ in the ultraviolet. It formed a 2,4-dinitrophenylhydrazone which exhibited a band at 360 $m\mu$ (ϵ 19,200) in the ultraviolet. Reduction of the carbonyl by the Wolff-Kishner method afforded an acid which was shown to be identical with an authentic sample of *trans*-bicyclo[2.2.1]-heptane-2,3-dicarboxylic acid.^{17,18} On the basis of these data, it seems certain that the compound isolated upon ozonolysis of compound VII must have the structure IV.¹⁹

Finally, the isomeric dimethylheptanones V and VI were prepared from the corresponding *exo* and *endo* adducts of 6,6-dimethylfulvene and maleic anhydride by reduction of the carboxyl functions and then by ozonolysis of the isopropylidene group. Reduction of the anhydrides of *exo*-acid VIII and *endo*-acid VII with lithium aluminum hydride²⁰ afforded good yields of stereochemically pure²¹ diols XIV and XV, respectively. On reaction with *p*-toluenesulfonyl chloride in pyridine solution, the diols were converted to the corresponding tosylates XVI and XVII, which were then smoothly



reduced by lithium aluminum hydride to the *exo-cis*-dimethyl olefin XVIII and *endo-cis*-dimethyl olefin XIX.^{20,22} Ozonolysis of the olefins, followed by reductive cleavage of the ozonides, provided

(16) E. T. McBee, O. K. Smith and H. E. Ungnade, *THIS JOURNAL*, **77**, 559 (1955).
 (17) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933).
 (18) The inversion of the *endo-cis*-dicarboxylic acid (IV) into the *trans* configuration is not unusual under the experimental conditions of the Wolff-Kishner reaction (cf. R. P. Linstead and S. B. Davis, *THIS JOURNAL*, **64**, 2006 (1942)).
 (19) The possibility of a skeletal rearrangement to a norcamphor derivative is precluded by the absorption in the infrared of the analogous *exo*-dihydrodicyclopentadienone (A) at 5.71 μ (unpublished results from this Laboratory).
 (20) G. A. Haggis and L. N. Owen, *J. Chem. Soc.*, 389 (1953).
 (21) D. S. Noyce and D. B. Denney, *THIS JOURNAL*, **72**, 5743 (1950); **74**, 5912 (1952).
 (22) H. M. Walborsky, *Helv. Chim. Acta*, **36**, 1251 (1953); G. Stork, E. E. van Tamelen, I. J. Friedman and A. W. Burgstahler, *THIS JOURNAL*, **75**, 384 (1953).



ketones V and VI. Each ketone formed a 2,4-dinitrophenylhydrazone and, unlike unsaturated polyaryl carbonyl bridge compounds, could be distilled at atmospheric pressure without decarbonylation. The infrared spectra of these ketones exhibited strong bands at 5.65μ (V) and 5.63μ (VI) which, along with those observed for IV, are in excellent agreement with the 5.64μ band reported by Allen and his co-workers.^{5,11}

Experimental²³

exo-cis-7-Isopropylidenebicyclo[2.2.1]-heptane-2,3-dicarboxylic Acid Anhydride.—The procedure of Alder and Rühmann was followed.¹³

endo-cis-7-Isopropylidenebicyclo[2.2.1]-heptane-2,3-dicarboxylic Acid Anhydride.—A modification of the method of Alder and Rühmann was employed. After 24 hours in ethyl ether (800 ml.) at 0° , 88 g. (0.83 mole) of 6,6-dimethylfulvene and 88 g. (0.90 mole) of maleic anhydride afforded 60 g. of relatively pure *exo* adduct, m.p. $130\text{--}135^\circ$, and 80 g. of a mixture of *exo* and *endo* adduct, m.p. $90\text{--}100^\circ$.¹⁴ The *exo-endo* mixture of m.p. $90\text{--}100^\circ$ was hydrogenated over Adams catalyst. After removal of the solvent the dihydro adduct, m.p. $125\text{--}150^\circ$, was washed with three 300-ml. portions of hot ligroin ($60\text{--}90^\circ$) to remove the *exo*-dihydro adduct. The residue was dissolved completely in hot ligroin ($90\text{--}120^\circ$) and was allowed to crystallize. The yield was 40 g. of colorless crystals, m.p. $168\text{--}170^\circ$ (reported 172°).¹³

endo-cis-7-Isopropylidenebicyclo[2.2.1]-heptane-2,3-dicarboxylic Acid (VII).—Eighteen grams of the *endo*-dihydro adduct, suspended in 125 ml. of 10% sodium carbonate solution, was heated under reflux for three hours. The reaction mixture was then cooled and acidified with hydrochloric acid solution. The solid obtained upon neutralization yielded after crystallization from alcohol-water 17.8 g. (91%) of colorless crystals, micro m.p. $163\text{--}164^\circ$ dec.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.28; H, 7.19. Found: C, 64.28; H, 7.32.

endo-cis-Bicyclo[2.2.1]-7-heptanone-2,3-dicarboxylic Acid (IV).—A solution of 4.0 g. (0.018 mole) of acid VII in 150 ml. of ethyl acetate at 0° was treated over a period of four hours with 0.47 cu. ft. of oxygen²⁴ containing 4% ozone.²⁵ Ozonolysis was continued until the uptake became negligible, as indicated by liberation of iodine in a potassium iodide solution through which the exit gases were passed. Reduction over Adams catalyst resulted in a hydrogen uptake of 450 ml. (97%). Upon evaporation of the solvent under vacuum 3.5 g. (99%) of crude material was isolated. This solid which was very soluble in water, was crystallized from that solvent with difficulty and was dried *in vacuo* over phosphorus pentoxide, micro m.p. $164\text{--}166^\circ$ dec.

Anal. Calcd. for $C_9H_{10}O_5$: C, 54.54; H, 5.09; neut. equiv., 99. Found: C, 54.40; H, 4.92; neut. equiv., 103.

No attempt was made to form a 2,4-dinitrophenylhydrazone from this product. In a previous experiment ozonolysis of the *endo*-dihydro adduct under the conditions described above provided an oily oxidation product which could not be induced to crystallize. Following the method of Sonntag and his co-workers²⁶ the 2,4-dinitrophenylhydrazone of this substance was prepared in small yield and was found to be the 2,4-dinitrophenylhydrazone of the 7-keto-diacid IV, rather than of the anhydride, m.p. $187\text{--}188^\circ$.

Anal. Calcd. for $C_{15}H_{14}N_4O_5$: C, 47.75; H, 3.74. Found: C, 47.87; H, 3.69.

Wolff-Kishner Reduction of 7-Keto-acid IV.—The reduction was carried out according to the general procedure of Huang-Minlon.²⁷ A solution of 2.0 g. of IV, 2 g. of so-

dium hydroxide and 1 ml. of 85% hydrazine hydrate in 25 ml. of diethylene glycol was heated under reflux for one hour. The condenser was then removed until the temperature of the reaction mixture reached 200° , whereupon the condenser was replaced and the mixture was allowed to reflux three hours longer. The solution was cooled, diluted with an equal volume of water, and extracted with ether. The aqueous layer was acidified with dilute hydrochloric acid, evaporated somewhat to remove diethylene glycol, and was extracted continuously with ether for four hours. Upon evaporation of the ether a solid separated which after crystallization from water yielded 0.6 g. of colorless crystals, m.p. $192\text{--}195^\circ$ (reported for *trans*-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid,¹⁷ $193\text{--}194^\circ$).

The infrared spectrum recorded in Nujol mull was identical in every respect with the spectrum of *trans*-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid prepared by the method of Alder and Stein.¹⁷

Hydrogen Peroxide Oxidation of the endo-cis-7-Isopropylidenebicyclo[2.2.1]heptane-2,3-dicarboxylic Acid Anhydride.—To a suspension of 40 g. (0.194 mole) of the *endo*-anhydride in 300 ml. of glacial acetic acid at 60° was added with stirring 80 g. of 30% hydrogen peroxide over a period of two hours. After 1.5 hours the adduct had dissolved completely. Stirring was discontinued and the reaction mixture was allowed to stand at 60° for 18 hours. After removal of the solvent under vacuum the viscous residue was diluted with water, whereupon 14.5 g. of solid precipitated. From repeated evaporations of the mother liquor there was obtained an additional 13.8 g. of solid. The yield of the hydroxy acetoxy derivative XII, after crystallization from water, was 25.4 g. (44%), micro m.p. $165\text{--}168^\circ$ dec.

Anal. Calcd. for $C_{14}H_{20}O_7$: C, 55.99; H, 6.71; neut. equiv., 150. Found: C, 55.88; H, 6.62; neut. equiv., 156.

endo-cis-Epoxydicarboxylic Acid XIII.—To a suspension of 21.7 g. (0.0724 mole) of XII in water was slowly added 10% sodium hydroxide solution until dissolution was complete. An additional 100 ml. of the alkaline solution was added and the solution was heated under reflux for eight hours. After standing overnight the reaction mixture was acidified with concentrated hydrochloric acid, was saturated with ammonium chloride, and was extracted continuously with ether for about 24 hours. Upon evaporation of the ether a solid was obtained; after crystallization from an acetone-ligroin mixture the yield was 16.0 g. (85%) of *endo-cis*-epoxy acid XIII, micro m.p. $171\text{--}172^\circ$ dec.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 60.00; H, 6.71; neut. equiv., 120. Found: C, 60.13; H, 6.65; neut. equiv., 125.

Reaction of Ozone upon Acid Ester IX.—A solution of 5.0 g. of IX¹ in 150 ml. of ethyl acetate at 0° was subjected to a stream of oxygen containing 4% ozone. Reaction was continued until the uptake became negligible. The ozonide in solution was then decomposed by hydrogenation at atmospheric pressure over 5% palladium-on-calcium carbonate. Hydrogen uptake was 70% of the theoretical amount. After removal of the solvent there remained a viscous oil which could not be induced to crystallize, along with some starting material. A 2,4-dinitrophenylhydrazone of the oil was prepared and was purified through repeated crystallizations from 95% ethanol, micro m.p. $160\text{--}166^\circ$.

Anal. Calcd. for $C_{17}H_{18}N_4O_5$: C, 50.25; H, 4.46. Found: C, 50.47; H, 4.96.

exo-cis-7-Isopropylidenebicyclo[2.2.1]heptane-2,3-dimethanol (XIV).—A suspension of 5.0 g. (0.13 mole) of lithium aluminum hydride in 400 ml. of absolute ethyl ether, contained in the pot of a Soxhlet extractor, was heated under reflux for one-half hour. Into the thimble of the extractor was placed 20.0 g. (0.097 mole) of the *exo*-dihydro-dimethylfulvene-maleic anhydride adduct. When extraction of the adduct by the solvent was complete, the reaction mixture was heated under reflux for about two additional hours and was then allowed to stand overnight at room temperature. Excess lithium aluminum hydride was decomposed by adding dropwise about 100 ml. of thoroughly wet ether, followed by careful addition of small amounts of water. The mixture was poured into 300 ml. of 10% hydrochloric acid and was shaken thoroughly. The ether layer was removed, the aqueous layer was extracted twice with small amounts of ether, and the combined extracts were dried over anhydrous sodium sulfate. Upon evaporation of the ether there was obtained a solid which after crystalli-

(23) All melting points except micro melting points and all boiling points are uncorrected. Microanalyses by Galbraith Laboratories, Knoxville, Tenn.

(24) Measured by the Wet Gas Meter manufactured by the American Meter Co.

(25) Ozone content measured by Dr. A. Brodhag of this Laboratory.

(26) N. O. V. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, *THIS JOURNAL*, **75**, 2289 (1953).

(27) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

zation from an alcohol-water mixture yielded 13.3 g. (70%) of colorless crystals, micro m.p. 135–136°.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.33; H, 10.11.

p-Toluenesulfonate of Diol XIV.—In 270 ml. of anhydrous pyridine at 0° was dissolved first 25.0 g. (0.127 mole) of the diol XIV and then 50.0 g. (0.263 mole) of *p*-toluenesulfonyl chloride. This solution, after standing at 0° for two days, was diluted with an equal volume of water, whereupon a solid separated. The solid was collected, washed well with water, and crystallized from 95% ethanol. The yield was 16.25 g. (63%), micro m.p. 128.5–129°.

Anal. Calcd. for $C_{26}H_{32}O_6S_2$: C, 61.88; H, 6.39. Found: C, 61.71; H, 6.37.

exo-cis-2,3-Dimethyl-7-isopropylidenebicyclo[2.2.1]heptane (XVIII).—Twenty grams (0.0398 mole) of the *exo-p*-toluenesulfonate derivative XVI, placed in the thimble of a Soxhlet extractor, was extracted over a period of about eight hours into a solution of 9 g. (0.24 mole) of lithium aluminum hydride in 500 ml. of absolute ethyl ether. The reaction mixture was allowed to stand overnight at room temperature and was worked up as before. Upon evaporation of the ether a crystalline product was obtained.

Twenty-four grams (0.047 mole) of the *exo-p*-toluenesulfonate derivative was treated in exactly the same fashion with 10 g. (0.26 mole) of lithium aluminum hydride in 500 ml. of absolute ether. The yields from both reactions were combined and distilled under vacuum. The yield was 12.6 g. (88%), b.p. 72–73° (8 mm.), micro b.p. 197° (754 mm.), m.p. 29–30°, n_D^{20} 1.4759.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.54; H, 12.20.

exo-cis-2,3-Dimethylbicyclo[2.2.1]-7-heptanone (V).—A solution of 5.0 g. (0.030 mole) of *exo-cis*-2,3-dimethyl-7-isopropylidenebicyclo[2.2.1]heptane (XVIII) in 150 ml. of ethyl acetate at 0° was treated with 0.7 cu. ft. of oxygen containing 4% ozone. Hydrogenation of the ozonide over Adams catalyst was attempted, but the rate of uptake was extremely slow. Only 27% of the theoretical amount of hydrogen was absorbed. The solvent was removed under vacuum and the viscous residue was treated for 10 minutes with 50 ml. of boiling water to which 1.0 g. of zinc dust had been added. The oily product was isolated through distillation with steam.

Six grams of the olefin XVIII in 150 ml. of ethyl acetate was treated as before with 0.8 cu. ft. of oxygen containing 4% ozone. The ozonide was worked up as before except that hydrogenation was omitted. The steam distillates were combined and extracted three times with ether. The ether solution was dried over sodium sulfate and was evaporated. The oily residue, upon distillation under vacuum, yielded 2.8 g. (30%) of a colorless oil, b.p. 78–82° (8 mm.), micro b.p. 207° (750 mm.), n_D^{20} 1.4668.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.45; H, 10.29.

The infrared spectrum exhibited a strong maximum in the carbonyl region at 5.65 μ .

The 2,4-dinitrophenylhydrazone was prepared in and crystallized from 95% ethanol, micro m.p. 172.5–173°.

Anal. Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70. Found: C, 56.82; H, 5.69.

endo-cis-7-Isopropylidenebicyclo[2.2.1]heptane-2,3-dimethanol (XV).—Forty-five grams (0.218 mole) of the *endo*-dihydrodimethylfulvene-maleic anhydride adduct was treated with a solution of 15 g. (0.395 mole) of lithium aluminum hydride in 800 ml. of absolute ethyl ether in exactly the same manner as was the *exo*-adduct. Upon removal of the solvent there remained a solid which after crystallization from an alcohol-water mixture yielded 32.0 g. (75%) of colorless crystals, micro m.p. 125.5–126°.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.66; H, 10.11.

p-Toluenesulfonate of Diol XV.—In 50 ml. of anhydrous pyridine at -10° was dissolved first 2 g. (0.0102 mole) of the diol XV and then 4 g. (0.021 mole) of *p*-toluenesulfonyl chloride. After the solution had stood at -10° for 24 hours, it was poured into 50 ml. of ice-water and was allowed to stand for ten minutes. The material which precipitated was collected, washed with water, and crystallized from 95% ethanol. The yield was 1 g. (20%), micro m.p. 128–129°.

Anal. Calcd. for $C_{26}H_{32}O_6S_2$: C, 61.88; H, 6.39. Found: C, 61.93; H, 6.24.

In another reaction 18 g. (0.092 mole) of the *endo*-diol XV was treated with 36 g. (0.19 mole) of *p*-toluenesulfonyl chloride in 350 ml. of anhydrous pyridine, at -10° , for one week. The reaction mixture was diluted with an equal volume of water and was allowed to stand for ten minutes. The solid which was collected, washed with water and then crystallized from 95% ethanol, gave 12.0 g. (26%) of colorless crystals, micro m.p. 137.5–138°.

Anal. Calcd. for $C_{26}H_{32}O_6S_2$: C, 61.88; H, 6.39. Found: C, 61.90; H, 6.31.

The infrared spectra of these two compounds measured in carbon tetrachloride solution were identical in every respect.

endo-cis-2,3-Dimethyl-7-isopropylidenebicyclo[2.2.1]heptane (XIX).—To 6.5 g. (0.17 mole) of lithium aluminum hydride dissolved in 500 ml. of anhydrous ethyl ether, was added by extraction from the thimble of a Soxhlet extractor 14.0 g. (0.0277 mole) of *endo-p*-toluenesulfonate XVII, m.p. 137.5–138°. After the addition was completed (about six hours) the reaction mixture was heated under reflux for an additional 16 hours. Excess lithium aluminum hydride was decomposed as before and the mixture was shaken with 300 ml. of 10% hydrochloric acid. The ether layer was removed, dried over anhydrous sodium sulfate and evaporated to dryness. The solid residue, after distillation under vacuum, yielded 3.6 g. (79%) of colorless crystals, micro m.p. 38–39°, b.p. 82° (10 mm.), micro b.p. 202° (749 mm.), n_D^{20} (supercooled) 1.4851.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.86; H, 12.31.

endo-cis-2,3-Dimethylbicyclo[2.2.1]-7-heptanone (VI).—A solution of 3.5 g. (0.0214 mole) of *endo-cis*-2,3-dimethyl-7-isopropylidenebicyclo[2.2.1]heptane (XIX) in 150 ml. of ethyl acetate was treated at 0° with 0.5 cu. ft. of oxygen containing 4% ozone. The solution of the ozonide over Adams catalyst was subjected to an atmosphere of hydrogen for 24 hours. Hydrogen uptake was 270 ml. (52.5%). The solvent was removed under vacuum and the oily residue was taken up in ether. The ether solution was washed with sodium carbonate solution, dried over sodium sulfate and evaporated. The residue, upon distillation under vacuum, yielded 0.9 g. (30%) of a colorless liquid, b.p. 74–76° (8 mm.), micro b.p. 202° (752 mm.), n_D^{20} 1.4712.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.46; H, 10.31.

The infrared spectrum exhibited a sharp maximum in the carbonyl region at 5.63 μ .

The 2,4-dinitrophenylhydrazone was prepared in 95% ethanol and purified chromatographically over alumina. Crystallization from 95% ethanol yielded an analytical sample, micro m.p. 146.5–149°.

Anal. Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70. Found: C, 56.79; H, 5.89.

Acknowledgment.—The authors are indebted to Miss Elizabeth A. Peterson for assistance in certain phases of this work and to the Duke University Research Council for a grant.

DURHAM, NORTH CAROLINA