chilled in an ice-bath and the solid which precipitated was filtered (8.6 g., m.p. 147–150°). The filtrate was diluted with water and an additional batch of solid was filtered (2.2 g., m.p. 102–109°), yield 88%.

One recrystallization of the higher melting material from benzene gave 8.0 g. of pale yellow plates, m.p. 149–150.5°. Two recrystallizations of the low melting product from ethyl acetate gave cubes, m.p. 123–125.5°. Bodforss[24a] reports the isolation, under similar conditions, of only one compound, m.p. 148°.

The previously unreported isomer, m.p. 123–125.5°, was analyzed.

Anal. Calcd. for $C_{15}H_{11}NO_4$: C, 66.92; H, 4.12; N, 5.20. Found: C, 66.45; H, 4.13; N, 5.20.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

The Synthesis of Bicyclo[2,2,2]-2,5-octadiene[1,2]

BY JACK HINE, JOHN A. BROWN, LEON H. ZALKOW, WILLIAM E. GARDNER AND MILDRED HINE

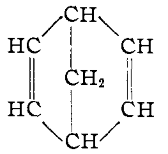
RECEIVED JULY 15, 1954

A synthesis is reported for bicyclo[2,2,2]-2,5-octadiene (II), a compound of particular interest because of unusual possibilities for interaction between non-conjugated double bonds. Two syntheses, one involving the dehalogenation of 2,3-dichlorobicyclo[2,2,1]-5-heptene and the other the dehydrohalogenation of 2-chlorobicyclo[2,2,1]-5-heptene, are reported also for the related compound bicyclo[2,2,1]-2,5-heptadiene (I). The preparation of II was accomplished by the dehydrohalogenation of a mixture of monochloro-2-bromobicyclo[2,2,2]octanes. The structures of I and II are proven by their reduction (by two moles of hydrogen) to the corresponding saturated hydrocarbons. In addition, II has been shown to form a crystalline tetrabromide and to yield ethylene and benzene upon pyrolysis. An improved method of preparing 1,3-cyclohexadiene also is reported.

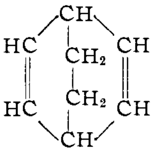
Introduction

There have been recently reported several studies of what we shall call *homoconjugation*, in which an olefinic double bond interacts with an atom which is separated from the nearest unsaturated carbon by one saturated carbon atom. These studies include the *i*-cholesteryl rearrangement,[3] rearrangements of dehydronorbornyl compounds to nortricyclene derivatives,[4] the acetolysis of 3-phenyl-2-butyl *p*-toluenesulfonate[5] and related reactions,[6] etc.

We were interested therefore in learning whether the effects of homoconjugation could be detected in the reactions of bicyclo[2,2,1]-2,5-heptadiene (I) and bicyclo[2,2,2]-2,5-octadiene (II).



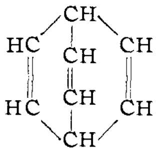
I



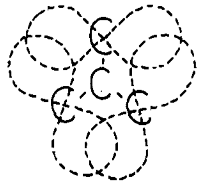
II

Such homoconjugation might reasonably be expected since the double bonds are so situated that their π-orbitals should overlap somewhat.[7]

We were further interested in learning whether this sort of interaction between double bonds on adjacent bridges of a bicyclic ring system might give aromatic character to bicyclo[2,2,2]-2,5,7-octatriene (III). A view of III from the top suggests that the π-orbitals of the double bonds might overlap enough for the formation of a somewhat cylindrical molecular orbital (containing six electrons) around the middle of the molecule.[7]



III



Top view of III

However, it may also be seen to be impossible to arrange the π-orbitals in a way which gives all overlapping lobes the same algebraic sign, as is said to be required.[7] Because this is the first case known to us in which the *sign* of an atomic orbital has been of such importance, compound III is of particular interest. While some derivatives of I and II such as the 2- and 3-carboxy compounds are known,[8] any study of interaction between the carbon–carbon double bond in these derivatives would be greatly complicated by the interaction of one of the double bonds with the functional group(s). Triptycene[9] can be thought of as the tribenzo derivative of III but the π-electrons in this compound may be too occupied with the benzenoid resonance to permit much interaction between adjacent bridges, although the difference in absorption spectra between triptycene and triphenylmethane has been attributed to such interaction.[9b]

Since this investigation was begun, Parham, Hunter, Hanson and Lahr have reported the preparation of a small amount of material which was probably the bicycloheptadiene, I.[10] This compound was prepared by the Chugaev degrada-

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[1] Sponsored by the Office of Ordnance Research, U. S. Army.

[2] Taken in part from the Ph.D. thesis of John A. Brown, 1954.

[3] C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946); S. Winstein and R. Adams, THIS JOURNAL, **70**, 838 (1948); R. G. Pearson, L. A. Subluskey and L. C. King, *ibid.*, **70**, 3479 (1948).

[4] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

[5] D. J. Cram, *ibid.*, **71**, 3863 (1949).

[6] *Cf.* E. M. Kosower, *Science*, **113**, 605 (1951).

[7] For a discussion of π-orbitals and their interactions to form multiple bonds and aromatic rings see C. A. Coulson, "Valence," Oxford University Press, London, 1952, Sections 4.7, 8.7 and 9.1.

[8] K. Alder, G. Stein, S. Schneider, M. Liebmann, E. Rolland and G. Schulze, *Ann.*, **525**, 183 (1936); O. Diels, K. Alder and H. Nienburg, *ibid.*, **490**, 236 (1931); K. Alder and H. F. Rickert, *Ber.*, **70B**, 1364 (1937).

[9] (a) P. D. Bartlett, M. J. Ryan and S. G. Cohen, THIS JOURNAL, **64**, 2649 (1942); (b) P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950).

[10] W. E. Parham, W. T. Hunter, R. Hanson and T. Lahr, *ibid.*, **74**, 5646 (1952).

tion of dehydronorborneol and it reacted with phenyl azide to give a product having the composition of one mole of I plus two of phenyl azide. These workers point out that I is not formed easily, attempted preparations by the acetate pyrolysis method and the Hofmann degradation of the quaternary ammonium hydroxide being unsuccessful.

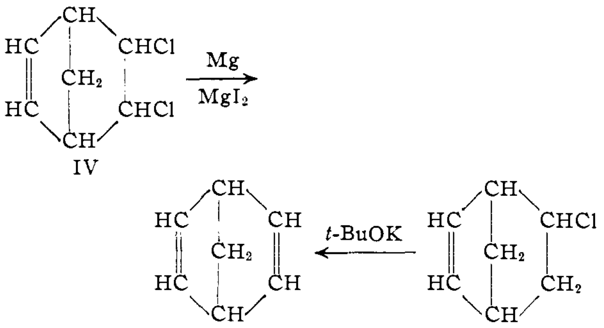
The use of I as an intermediate in preparing the insecticide Aldrin is reported in a patent by Lidov.[11] In this patent the preparation of I is not described but is said to be the subject of a pending patent application.[12]

We have learned also that the interaction between the double bonds of I has been studied in some detail by Dr. Saul Winstein who has found evidence for homoconjugation in several cases.[13] We have therefore given I no attention in this regard and plan to study only II and III. We did, however, continue studying methods for synthesizing I for use as "model" reactions for the synthesis of II and III because the commercial availability of dicyclopentadiene makes most bicyclo[2,2,1]heptane derivatives more readily obtainable than the corresponding bicyclo[2,2,2]octane compounds.

Results and Discussion

The attempted dehydration of dehydronorborneol being unsuccessful, we next tried to dehalogenate 2,3-dichlorobicyclo[2,2,1]-5-heptene (IV). Sodium iodide in acetone gave no reaction, but dechlorination was accomplished by use of a mixture of magnesium and magnesium iodide in *n*-butyl ether.

The bicycloheptadiene was prepared also by the dehydrohalogenation of 2-chlorobicyclo[2,2,1]-5-heptene (V). Quinoline was not useful for this purpose, but with potassium *t*-butoxide a 25% yield was obtained.



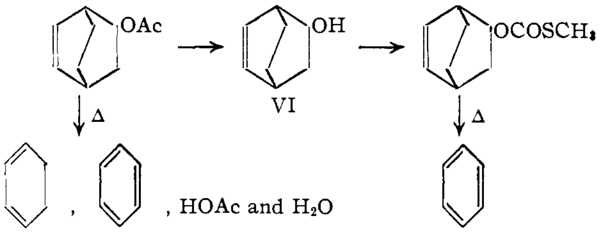
The hydrocarbon thus prepared was a colorless, mobile liquid boiling at 89.5°. Its structure is established by its methods of synthesis, its elemental analysis and its catalytic hydrogenation (requiring two moles of hydrogen) to bicyclo[2,2,1]-heptane.

Since most of the useful methods of entry into the bicyclo[2,2,2]octane series involve the Diels–Alder addition of various unsaturated compounds to 1,3-cyclohexadiene, we were interested in finding a convenient method for preparing this compound in fairly large quantities on a laboratory scale. We have found that the dehydrohalogenation of cyclohexene dibromide by quinoline[14] yields more cyclohexene and benzene than cyclohexadiene.[15] On the other hand, while the method of Hofmann and Damm, in which most of the diene is obtained by the potassium bisulfate catalyzed de-ethanolation of 3-ethoxycyclohexene,[16] gives a much purer product, the preparation requires an extra step and involves a somewhat tedious separation of ethanol from the product.

We have found that triethanolamine or tri-*n*-butylamine gives no better a product than does quinoline, but that with sodium hydroxide in ethylene glycol solution, cyclohexene dibromide may be transformed rapidly and in good yield to 1,3-cyclohexadiene of about 80% purity. Since the benzene and cyclohexene present as impurities do not interfere with the subsequent Diels–Alder reactions this material is satisfactory for our purposes.

The synthesis of the bicyclooctadiene II was first attempted by methods analogous to those which were successful in the preparation of I. The addition of *trans*-1,2-dichloroethylene to cyclohexadiene gave a poor yield of a product boiling over a fairly narrow range at about the expected temperature for 2,3-dichlorobicyclo[2,2,2]-5-octene. Its chemical analysis and certain other properties, however, suggested that the desired product was mixed with a somewhat larger quantity of dicyclohexadiene. No product was isolated when this impure product was treated with magnesium–magnesium iodide.

We also attempted to prepare II from the alcohol VI by the acetate pyrolysis and Chugaev methods. Only benzene, cyclohexadiene, acetic acid and water were identified as products of the acetate pyrolysis, while only benzene was isolated in the Chugaev reaction.



The oxidative bisdecarboxylation reaction of Doering, Farber and Sayigh[17] on bicyclo[2,2,2]-5-octene-2,3-dicarboxylic anhydride also gave us none of compound II. We next tried a dehydrohalogenation method. Bicyclo[2,2,2]-2-octene was prepared by the Diels–Alder addition of ethylene to cyclohexadiene, and to the octene was added hydrogen bromide.[18] The resultant 2-bromobicyclo[2,2,2]-octane was chlorinated with sulfuryl chloride. The mixture of monochlorides, separated from polychlorides by fractionation, should contain a consid-

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[11] R. E. Lidov, U. S. Patent 2,635,977 (April 21, 1953) assigned to Shell Development Company.

[12] Hyman, Freireich and Lidov, Patent Application, U. S. Serial No. 45,574.

[13] S. Winstein, private communication.

[14] A. W. Crossley, *J. Chem. Soc.*, **85**, 1403 (1904).

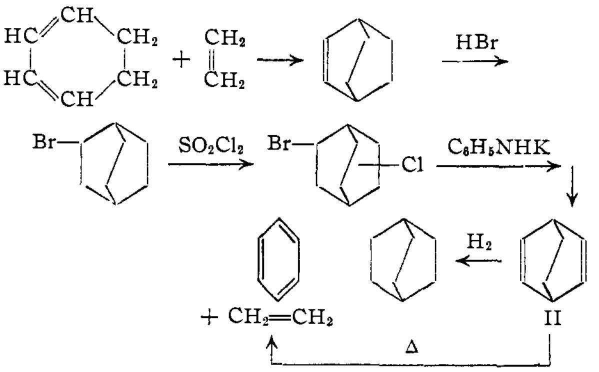
[15] *Cf.* K. W. F. Kohlrausch and R. Seka, *Ber.*, **68B**, 528 (1935).

[16] F. Hofmann and P. Damm, *Chem. Zentr.*, **97**, I, 2342 (1926); *C.A.*, **22**, 1249 (1928).

[17] W. von E. Doering, M. Farber and A. Sayigh, THIS JOURNAL, **74**, 4370 (1952).

[18] W. von E. Doering and M. Farber, *ibid.*, **71**, 1514 (1949).

erable percentage of the 5- and 6-chloro compounds, the only isomers capable of dehydrohalogenation to II, due to the tendency in free radical chlorination to avoid substitution on the same carbon as, or one adjacent to, a halogen atom already present.[19] We were unable to isolate any II from the action of potassium *t*-amyloxide on the mixture of monochloro-2-bromobicyclo[2,2,2]-octanes, but reaction with potassium anilide gave a small yield of II and also benzene and ethylene.



The structural formula assigned II is in agreement with its elemental analysis, physical properties and method of synthesis, but further evidence was obtained as follows. The catalytic hydrogenation of II required two moles of hydrogen and produced bicyclo[2,2,2]octane. The addition of bromine gave a crystalline tetrabromide. The infrared spectrum of II (Fig. 1) shows maxima at 6.13 and 6.29 μ, in the characteristic region for carbon–carbon double bonds. Upon pyrolysis, II underwent a reverse Diels–Alder reaction to yield benzene and ethylene. The fact that this pyrolysis does not occur at a reasonable rate when II is distilled or even heated with potassium anilide in aniline or in decalin, but requires a dull red glowing wire, suggests that the benzene and ethylene by-products in the preparation of II do not arise from its decomposition.

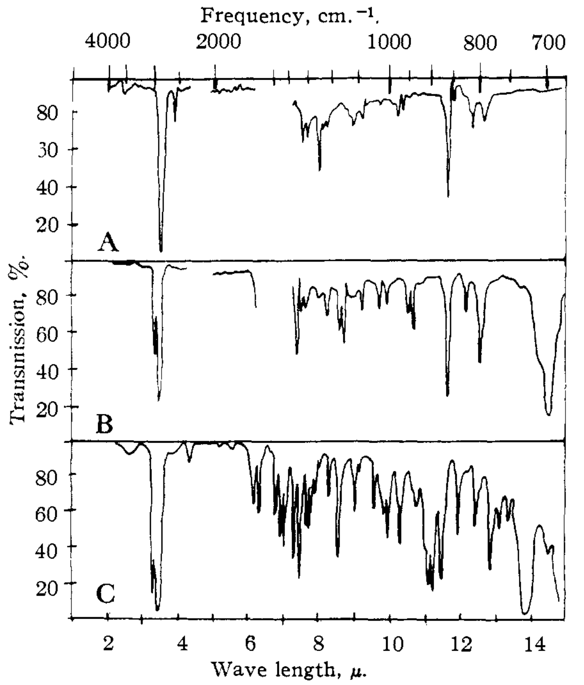
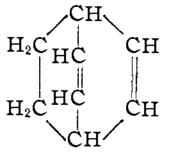
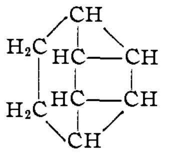


Fig. 1.—Infrared spectra of: A, bicyclo[2,2,2]octane in carbon disulfide; B, bicyclo[2,2,2]-2-octene in carbon disulfide; C, bicyclo[2,2,2]-2,5-octadiene.

These data, however, do not distinguish unequivocally between the structural formulas IIa and IIb or even make clear whether IIa and IIb are structures for two different compounds or merely two different resonance structures contributing to the total structure of one compound.[20] The problem thus stated in terms of valence bond resonance is essentially the one we already described in terms of atomic and molecular orbitals in the introduction. We hope to work toward its answer, the nature of the interaction between double bonds on adjacent rings of a bicyclic ring system, by further studies on II and by attempting to prepare and study III.[21]



IIa



IIb

Experimental[22]

Attempted Dehydration of Dehydro-α-norborneol.—Dehydro-α-norborneol prepared from its acetate by the method of Alder and Rickert[23] was heated with phosphorus pentoxide in xylene solution. Distillation of the reaction mixture gave no product more volatile than xylene.

Attempted Dehalogenation of 2,3-Dichlorobicyclo[2,2,1]-5-heptene.—A solution of 2,3-dichlorobicyclo[2,2,1]-5-heptene[23] and sodium iodide in acetone was refluxed for three hours and allowed to stand for several days. No precipitate of sodium chloride or iodine color was formed.

Bicyclo[2,2,1]-2,5-heptadiene (I). A. From 2,3-Dichlorobicyclo[2,2,1]-5-heptene.—The dehalogenation reagent was prepared in a manner similar to that described by Summerbell and Umhoefer[24] by adding 198 g. (0.78 mole) of iodine to 48.6 g. (2.0 moles) of magnesium in 630 ml. of di-*n*-butyl ether. To this refluxing solution was added 132 g. (0.81 mole) of 2,3-dichlorobicyclo[2,2,1]-5-heptene[23] dropwise with stirring. The contents of the flask were then distilled to dryness and the distillate fractionally redistilled. Between 86 and 89° (atm.) 19 g. (25% yield) of product was obtained, which upon refractionation gave 14.4 g., b.p. 89–89.5° (atm.), $n^{26}\mathrm{D}$ 1.4670, d^{26}_{4} 0.8992. According to Lidov, bicyclo[2,2,1]-2,5-heptadiene boils in the range 85–90° at 630 mm.[11]

Anal. Calcd. for C_7H_8: C, 91.25; H, 8.75. Found: C, 91.20; H, 8.95.

B. From 2-Chlorobicyclo[2,2,1]-5-heptene.—Thirty grams (0.233 mole) of 2-chlorobicyclo[2,2,1]-5-heptene[23] was added to 300 ml. of *t*-butyl alcohol in which 19.5 g. (0.5

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[19] D. V. Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 658 (1937); *C. A.*, **31**, 5755¹ (1937); M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939); A. L. Henne and J. B. Hinkamp, *ibid.*, **67**, 1197 (1945).

[20] ADDED IN PROOF.—S. J. Cristol and R. L. Snell (*ibid.*, **76**, 5000 (1954)) have reported the existence of two distinct compounds of the type of IIa and IIb for the 2,3-dicarboxylic acid derivative of I.

[21] We should like to suggest for III the name *klovosene* (from the Greek Κλωβός, bird-cage) which we have been using informally for the compound for several years.

[22] Melting points and boiling points uncorrected. Analyses by Clark Microanalytical Laboratory, Urbana, Ill.

[23] K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1940).

[24] R. K. Summerbell and R. R. Umhoefer, THIS JOURNAL, **61**, 3016, 3020 (1939).

mole) of potassium had been dissolved. Since no potassium chloride had been precipitated after the solution was refluxed for an hour and then allowed to stand for a week, the material was slowly distilled through a fractionating column. The first distillate was essentially pure *t*-butyl alcohol, but as the pot temperature rose a reaction appeared to take place and the odor of the bicycloheptadiene became apparent. The last 40 ml. of distillate was therefore diluted with a large excess of water and an oily layer separated. This oil was dried over calcium chloride, mixed with some *o*-xylene (to serve as a distillation base) and fractionally distilled. The fraction boiling at 89.5–90° weighed 5.4 g. (25% yield) and its infrared spectrum was identical to that of the material whose preparation is described above.

Compound I was found to require 1.97 ± 0.1 moles of hydrogen for reduction by Adams catalyst in ethanol to material identical in boiling point, odor and infrared spectrum to bicyclo[2,2,1]heptane prepared by the method of Roberts, Urbanek and Armstrong.[25]

1,3-Cyclohexadiene.—All of our preparations of cyclohexadiene utilized cyclohexene dibromide as the starting material. This material was prepared by adding bromine directly to cyclohexene containing a small amount of ethanol or acetic acid and kept below 0°. By use of a Dry Ice cooling bath the addition could be carried out relatively rapidly.

Two hundred seventy-five grams (1.7 moles) of cyclohexene dibromide was added to 875 g. (4.73 moles) of tri-*n*-butylamine at 200°. The crude product was distilled continuously from the reaction mixture and when fractionated gave 95 g. (70% yield, if pure diene) of material boiling at 80°. The refractive index showed that this material probably contained at least 50% cyclohexene. The use of quinoline[15] gave results similar to this and a smaller yield of even less pure product was obtained with triethanolamine.

Sodium hydroxide in ethylene glycol solution (we were actually dealing with the sodium salt of ethylene glycol, no doubt) proved to be the most suitable dehydrohalogenating agent for our use. The method described below is the result of a considerable, but by no means complete, search for the optimum operating conditions. Four liters of ethylene glycol was placed in a 12-l. three-necked flask equipped with a vapor-tight stirrer, a thermometer whose bulb was in the liquid, a dropping funnel, and a 36-in. fractionating column, 1 in. in diameter and packed with glass helices. Two kilograms (50 moles) of sodium hydroxide was added and the flask was heated and its contents stirred until they reached 230°, when about 700 ml. of water had been distilled from the solution. Stirring is needed to prevent the dangerously sudden and exothermic solution of the alkali at about 140° and to break up the foam produced above 200°. At temperatures much above 230° the evolution of hydrogen gas from the reaction mixture becomes a major competing reaction. At this point 4 kg. (16.5 moles) of cyclohexene dibromide was added over a period of three hours, while a mixture of crude product and water distilled from the reaction mixture. The temperature in the reaction flask was kept between 220 and 230° and that in the head of the distilling column below 100°. The 1300 g. of organic layer in the distillate was separated from a similar amount of water, dried over calcium chloride and fractionally distilled. Between 79 and 82°, 980 g. was collected. From the refractive index ($n^{24}\text{D}$ 1.4689) and infrared spectrum it was estimated that the material was 81% cyclohexadiene, 15% cyclohexene and 4% benzene. The yield of cyclohexadiene was therefore 60%.

The use of sodium hydroxide in triethanolamine solution gave no better results, and furthermore this method has the disadvantage of requiring a larger amount of a more expensive solvent to dissolve a given amount of sodium hydroxide. Diethylene glycol may be substituted for ethylene glycol as the reaction solvent, provided at least 3 ml. of glycol per gram of sodium hydroxide is used. If a smaller ratio of diethylene glycol to alkali is used a dangerously exothermic reaction between the two takes place at temperatures somewhat above 200°.

Attempted Preparation and Dehalogenation of 2,3-Dichlorobicyclo[2,2,2]-5-octene.—Sixteen grams of 50% 1,3-cyclohexadiene (0.1 mole) and 9.7 g. (0.1 mole) of *trans*-dichloroethylene were heated in a sealed glass tube to 180–220° for 22 hours. Distillation of this reaction mixture yielded 3.5 g. of material boiling at 90–93° (10 mm.). From the boiling point, method of preparation and analysis, the mixture appeared to contain 2,3-dichlorobicyclo[2,2,2]-5-octene and a somewhat larger amount of cyclohexadiene dimer.[16,26] Variations in the reaction temperature, time and ratio of reactants gave no significant improvement in this method.

Attempted dehalogenation of 30 g. of the impure material prepared as described above by use of 12 g. of magnesium and 40 g. of iodine in a procedure like that described for I gave no significant quantity of material more volatile than the di-*n*-butyl ether solvent.

2-Acetoxybicyclo[2,2,2]-5-octene and its Pyrolysis.—This compound was prepared by a method like that of Alder and Rickert[28] who give few experimental details and none of the physical properties of the product, however. A small amount of hydroquinone, 175 g. of 81% 1,3-cyclohexadiene (1.77 moles) and 190 g. (2.21 moles) of vinyl acetate was kept around 180° for five days in a high pressure reaction vessel. Fractional distillation yielded 109 g. (37% yield) of product, b.p. 125–130° (44 mm.), $n^{27}\text{D}$ 1.5020. Decomposition of this acetate did not occur at a reasonable rate at its boiling point, 217° (atm.), and so it was distilled through a tube packed with glass helices and wrapped with wire heated to a dull red color. The product was a bright yellow liquid which upon fractional distillation gave appreciable amounts only of a wet mixture of benzene and cyclohexadiene, b.p. 75–77° (identified by infrared spectra) and of acetic acid, b.p. 110–113° as products boiling below 180°.

Chugaev Degradation of Bicyclo[2,2,2]-5-octen-2-ol.—Thirty-six grams (0.29 mole) of bicyclo[2,2,2]-5-octen-2-ol[27] and 11.4 g. (0.29 mole) of potassium were heated in 400 ml. of freshly distilled decalin. When all of the potassium had reacted 200 ml. of ether and 40 g. of carbon disulfide were added, and after two hours of stirring at reflux 90 g. of methyl iodide was added. The ether and excess carbon disulfide and methyl iodide were removed by fractionation and the xanthate was pyrolyzed by distilling the residue to dryness. The distillate was washed with aqueous alkali and mercuric chloride to remove carbonyl sulfide and mercaptans, then dried and fractionally distilled. Fraction 1, 2.5 ml., b.p. 44–77°, appeared to be only wet benzene and fraction 2, 5.5 ml., b.p. 77–78°, essentially pure benzene from their infrared spectra. No other fraction was found below the boiling point of decalin.

Attempted Bisdecarboxylation of Bicyclo[2,2,2]-5-octene-2,3-dicarboxylic Anhydride.—Following the general procedure of Doering, Farber and Sayigh,[17] 6.9 g. (0.038 mole) of bicyclo[2,2,2]-5-octene-2,3-dicarboxylic anhydride[28] in 75 ml. of decalin was heated to reflux with 30 g. of lead dioxide. When the evolution of carbon dioxide had stopped the liquid was decanted, the solid washed with decalin and then added to the decanted liquid. Distillation of the decalin solution yielded no material boiling below 185°.

Bicyclo[2,2,2]-2-octene.—A 1500-ml. capacity Aminco high pressure reaction vessel containing 450 ml. of cyclohexadiene prepared as described (3.75 moles of pure diene) was charged with ethylene to a pressure of 750 p.s.i.[29] The reaction vessel was kept at 280 ± 30° for 34 hours and then cooled and opened. Distillation of the contents yielded 95 ml. of material boiling below 130° (largely at 80–85°) and 218 g. (54% yield) of material, b.p. 130–135° (largely 134°), m.p. 110–113°. Seka and Tramposch state that bicyclo-[2,2,2]-2-octene melts at 113–114°[30] and although Doering, Farber and Sayigh list a m.p. of 141–144° they may have intended to write 111–114° since they quoted Seka and Tramposch's m.p. as 143–144°.[17]

Monochloro-2-bromobicyclo[2,2,2]octane.—Seventy-five grams (0.4 mole) of 2-bromobicyclo[2,2,2]octane, prepared by the addition of hydrogen bromide to bicyclo[2,2,2]-2-octene,[18] 102 g. (0.75 mole) of sulfuryl chloride and a small

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[25] J. D. Roberts, L. Urbanek and R. Armstrong, THIS JOURNAL, **71**, 3049 (1949).

[26] K. Alder and G. Stein, *Ann.*, **496**, 197 (1932).

[27] W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1954).

[28] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

[29] The analogous Diels–Alder addition of cyclohexadiene to propylene has been described by G. Calingaert, H. Soroos and H. Shapiro, *Ind. Eng. Chem.*, **36**, 1055 (1944). ADDED IN PROOF.—H. M. Walborsky and D. F. Loncrini (THIS JOURNAL, **76**, 5396 (1954)) have reported this method of preparing the bicyclooctene.

[30] R. Seka and O. Tramposch, *Ber.*, **75B**, 1379 (1942).

amount of benzoyl peroxide were mixed and the solution allowed to reflux for four hours as its temperature increased from 75 to 190°. The material was then distilled, and the 71 g. of distillate collected up to 190° at 50 mm. was fractionally redistilled in vacuum. Thirty-eight grams (42% yield) of low melting solid was obtained, b.p. 125–130° (15 mm.). The product appears to be largely a mixture of the monochlorides.

Anal. Calcd. for $C_8H_{12}ClBr$: mmoles of halogen per g. 8.95; for $C_8H_{11}Cl_2Br$: 11.63. Found: 9.17, 9.32.

Reaction of Monochloro-2-bromobicyclo[2,2,2]octane with Potassium *t*-Amyloxide.—One hundred grams of *t*-amyl alcohol in which 11 g. (0.29 mole) of potassium had been dissolved and 22.2 g. (0.1 mole) of monochloro-2-bromobicyclo[2,2,2]octane was refluxed in a 200-ml. flask attached to a gas collection apparatus. After 40 hours about 400 ml. of gas, shown by its infrared spectrum to be ethylene, had been evolved. A titration at this time showed that 0.164 mole of base had been used up. The reaction mixture was shaken with water and the organic layer separated, dried and fractionally distilled. When the *t*-amyl alcohol had been removed the pot temperature rose above 170° without the distillation of any additional material.

Bicyclo[2,2,2]-2,5-octadiene.—Twenty grams (0.51 mole) of potassium and 250 ml. of aniline were placed in a three-necked flask equipped with a vapor-tight stirrer, thermometer, dropping funnel and Claisen distilling head leading through a condenser, receiver and drying tube to a gas collection apparatus. The system was swept with nitrogen and the aniline heated to reflux to dissolve the potassium. Then 38 g. (0.17 mole) of monochloro-2-bromobicyclo[2,2,2]-octane in about 20 ml. of aniline was added slowly to the gently refluxing solution. Some material distilled during the addition of the chlorobromide, and when the addition was complete distillation was continued until the distillate temperature reached 170°. The distillate was washed with cold hydrochloric acid to remove the aniline and then dried over Drierite and fractionally distilled. At about 30° (155 mm.), 4 g. (30% yield) of benzene was collected and at 59–61° (155 mm.), 1.5 g. (8% yield) of product was obtained. One liter of gas (24% yield), shown by its infrared spectrum to be ethylene containing a little acetylene, also was produced in the reaction.

The product of this and other similar preparations was found to have the properties: b.p. 126–127° (atm.), $n^{23.5}D$ 1.4912, d^{32}_4 0.9171.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.54; H, 9.54.

Reactions of Bicyclo[2,2,2]-2,5-octadiene (II).—Bromine was added to II until the red color was no longer discharged, and the resultant oil was cooled in Dry Ice until it crystallized. The crystals were washed with ethanol, recrystallized from ether–ethanol and then from hexane to yield white crystals, m.p. 103–103.5°.

Anal. Calcd. for $C_8H_{10}Br_4$: C, 22.56; H, 2.37; Br, 75.07. Found: C, 22.79, 22.75; H, 2.49, 2.52; Br, 74.71, 74.76.

When II was refluxed alone, in decalin or in aniline in which potassium had been dissolved for a time (30 minutes) longer than that which had been used in its synthesis, little, if any, gas was formed. However, when about 0.2 g. of II was refluxed under nitrogen so that the vapor came in contact with a wire coil heated to a dull red color, about 25 ml. of gas, shown by its infrared spectrum to be ethylene containing a little acetylene, was produced. The first few drops of distillate from the remaining liquid was shown, also by its infrared spectrum, to contain benzene.

Compound II was found to require 2.0 ± 0.2 moles of hydrogen for complete reduction. The white crystalline product had an infrared spectrum identical to the bicyclo-[2,2,2]octane prepared by reduction of bicyclo[2,2,2]-2-octene.[30]

Infrared Spectra.—The infrared spectra were determined using a Perkin–Elmer instrument, model 21. Samples were run in a 0.1-mm. cell and those run in solution were compensated with pure solvent in the same size cell.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Seven-membered Ring Compounds. IX. Benzosuberoneglyoxylates

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Additional examples of enol lactone formation in the condensation of dimethyl oxalate with 1,2,3-trimethoxy-, 1-methyl- and 2,3-dimethylbenzosuberone in contrast to the normal condensation with 1,4-dimethoxy- and 1,4-dimethylbenzosuberone confirm the importance previously assigned to the substituent in position 4.

The sodium methoxide-catalyzed condensation of dimethyl oxalate with benzosuberone was previously reported[2] to yield the expected methyl glyoxylate (Ia) in the case of 2,3,4-trimethoxybenzosuberone (IIa) whereas 2,3-dimethoxy-, 8-methyl- and benzosuberone itself under the same conditions gave enol lactones similar to III.

In the present work, five additional substituted benzosuberones have been prepared and condensed with methyl oxalate. Those benzosuberones with a methoxyl or a methyl group in the 4-position formed methyl glyoxylates whereas those with hydrogen in the 4-position formed enol lactones.

The desired benzosuberones were obtained by a series of steps starting with acylation of 1,4-dimethoxy-, 1,2,3-trimethoxy-, 1,2-dimethyl- and 1,4-dimethylbenzenes, respectively, with γ-carbethoxybutyryl chloride.[3] The aroylbutyric acids obtained were reduced to the corresponding valeric acids and these on treatment with polyphosphoric acid gave the benzosuberones IIb, IId, IIe and IIf. 1-Methylbenzosuberone was prepared from *o*-tolualdehyde by a published method.[4]

The known 1,4-dimethylbenzosuberone[5] (IIf) was of particular interest in that heretofore enol lactone formation in the glyoxylation reaction had been blocked only by methoxyl groups. Caution concerning the structure of this 1,4-dimethylbenzosuberone is indicated due to the reported cases of migration of groups in hot polyphosphoric acid cyclizations.[6] 1,4-Dimethylbenzosuberone gave a glyoxylate which was an oil. Since the known methyl benzosuberoneglyoxylates all melt below 120° with one reported as an oil[2] whereas the enol lactones are higher melting solids, all being above 112°, the product in this case is formulated as If. The py-

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[1] Taken in part from the Master's Dissertation and the Doctoral Dissertation of C. L. Anderson and F. E. Walker, respectively.

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