

The Synthesis of 1,4-Dichlorobicyclo[2.2.1]heptane¹

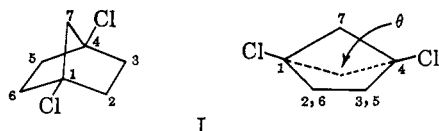
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1,4-Dichlorobicyclo[2.2.1]heptane has been prepared by several routes and its structure has been established rigorously.

There has appeared recently a scheme for calculating internuclear distances and dipole moments of bicyclo[1.1.1]pentane, bicyclo[2.2.1]hexane, and bicyclo[2.2.1]heptane derivatives.³ Because of the widespread interest in these bicyclic systems, any refinement of the method or numerical values would be of great practical value. An excellent starting point for checking and improving the method would be the unknown 1,4-dichlorobicyclo[2.2.1]heptane (I), since its dipole moment is extremely sensitive to the angle of intersection of the C-Cl bond vectors. This paper describes the preparation of I and its structure proof. A subsequent paper will report the dipole moment of I and related compounds.

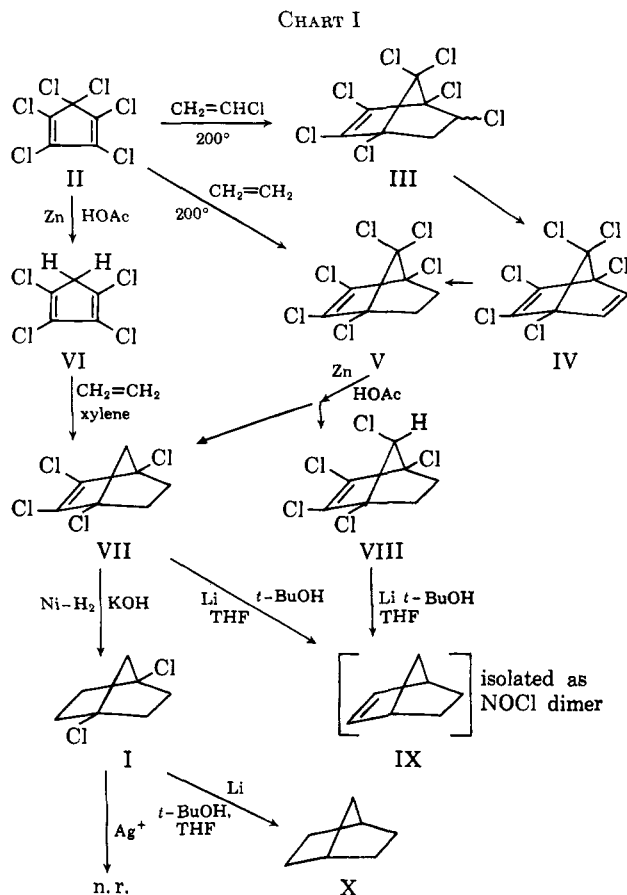


Preparation of 1,4-Dichlorobicyclo[2.2.1]heptane (I).

The general plan for the preparation of the dichloride (I) was to prepare a polychlorinated derivative of norbornane from which all but the bridgehead chlorines would be removed by taking advantage of the low relative reactivity of bridgehead halogens. As it developed 1,2,3,4-tetrachlorobicycloheptene-2 (VII, see Chart I) could be converted into the desired dichloride in one simple step so that the synthetic problem was reduced to finding a practical synthesis of VII. The preparation of VII was carried out by several routes from the readily available hexachlorocyclopentadiene (II) as outlined in Chart I.

One of these routes was to remove two chlorines from II to give the known 1,2,3,4-tetrachlorocyclopentadiene (VI),⁴ which was then converted to the desired tetrachloride (VII) in 20% yield by bubbling ethylene through a solution of VI in refluxing xylene. The structure of VII follows in part from its mode of preparation and correct analysis. Corroborative evidence is provided by removal of all four of the chlorines using the Winstein reduction procedure⁵ to give bicycloheptene (isolated as its nitrosyl chloride dimer). Further evidence for the structure of VII is provided by synthesis of it from other known compounds as shown in Chart I and described below.

Another route to VII was by way of the known heptachloride^{6,7} III which was converted into the previously described hexachloride IV by the procedure outlined by



Kleinman⁶ followed by catalytic reduction to V. The over-all yield of V for these three steps was 49%.

An alternate preparation of I suggested by the work of Schmerling⁸ and Hoch⁹ was to bubble ethylene for 24 hr. into II that was maintained at 200°. In this manner 94% yields of pure V could be prepared on a large scale with simple apparatus.

The two bridge chlorines of V were removed by treatment with zinc and acetic acid¹⁰ to give a low yield (29%) of the desired intermediate VII. In addition to VII a compound containing five chlorines was isolated in 40% yield. The structure of the pentachloro compound was assigned as VIII by the following evidence. First, it was established that the bicycloheptane skeleton was present by conversion of VIII into the same nitrosyl chloride dimer that had been obtained previously from VII. An infrared spectrum of VIII

(1) This work was supported by the National Science Foundation.

(2) Taken from the dissertation submitted by J. G. Zajacek to Cornell University for the Ph.D. degree, Sept., 1962.

(3) C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960); see also H. Krieger, *Suomen Kemistilehti*, **B31**, 348 (1958).

(4) A. Roedig and L. Hornig, *Ber.*, **88**, 2003 (1955); A. A. Danish, M. Silverman, and Y. A. Tajiima, *J. Am. Chem. Soc.*, **76**, 6144 (1954).

(5) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960).

(6) U. S. Patent 2,655,513 (Oct. 13, 1953); M. Kleinman, *Chem. Abstr.*, **48**, 10,773 (1954); U. S. Patent 2,736,730 (Feb. 28, 1956); M. Kleinman *Chem. Abstr.*, **50**, 10,780 (1956).

(7) U. S. Patent 2,717,851 (Sept. 13, 1955); R. E. Lidov, *Chem. Abstr.*, **50**, 2914 (1956).

(8) U. S. Patent 2,881,223 (April 7, 1959); L. Schmerling, *Chem. Abstr.*, **53**, 17,013 (1959).

(9) P. E. Hoch, *J. Org. Chem.*, **26**, 2066 (1961).

(10) S. B. Soloway, A. M. Daniana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Am. Chem. Soc.*, **82**, 5377 (1960).

showed a band at 6.35μ , which is characteristic of a structural unit containing two chlorines on a double bond.¹⁰ This same band was present in compounds III, IV, V, and VII, and absent in I. The integrated n.m.r. spectrum indicated that VIII had a lone hydrogen on a carbon bearing a chlorine and that VIII had four other hydrogens arranged to give a characteristic A_2B_2 pattern. The *syn* relationship of the chlorine at C-7 was assigned primarily because VIII failed to be reduced over Adams catalyst. A similar inertness to reduction was observed for V, which also has a chlorine *syn* to the $Cl-C=C-Cl$ group; compound VII without the blocking Cl is readily reduced over Adams catalyst. The *syn* assignment is considered tentative until a detailed n.m.r. analysis, in progress, has been completed.

Compound VII was converted to the dichloride (I) in 82% yield by reduction with Raney nickel in the presence of excess base. This reaction probably proceeds by a consecutive series of reductions and eliminations. The structure of I was established in the following manner. Reduction of I with lithium and *t*-butyl alcohol, in tetrahydrofuran, gave norbornane, thereby establishing the skeleton of I. Analytical data indicated the presence of two chlorine atoms. The lack of reactivity of I when heated with alcoholic $AgNO_3$ at 100° for 30 hr. showed that these chlorines were in bridgehead (inert) positions. An n.m.r. spectrum of I showed two peaks in a 1:4 ratio in the methylene region and no peaks for tertiary hydrogens or hydrogens adjacent to a chlorine atom.

Conclusions

1,4-Dichlorobicyclo[2.2.1]heptane can be prepared by several synthetic sequences. The preferred route to the dichloride is the sequence $II \rightarrow V \rightarrow VII \rightarrow I$. These reactions can be run on a large scale and only one careful distillation is required. The over-all yield of I from II is 22%.

Experimental

1,2,3,4,5,7,7-Heptachlorobicyclo[2.2.1]heptane-2 (III).—Compound III was prepared from hexachlorocyclopentadiene and vinyl chloride following the procedure of Kleinman⁶ modified only by passing in the vinyl chloride for 24 hr. instead of the specified 14 hr. After the unreacted hexachlorocyclopentadiene had been removed by distillation, the product in the distillation pot solidified on cooling. It was purified by sublimation at 100° and 2.5 mm. to give a 71% yield of III, m.p. $147.5-162.5^\circ$, lit.⁶ m.p. $125-136^\circ$.

1,2,3,4,7,7-Hexachlorobicyclo[2.2.1]heptadiene-2,5 (IV).—Compound IV was prepared by a procedure closely related to that of Kleinman.⁶ A solution of 432 g. (1.27 moles) of heptachloride III and 73.7 g. (1.31 moles) of potassium hydroxide (85%) in 1300 ml. of absolute ethanol was heated under reflux for 3 hr. The ethanol was removed by distillation through a 30-cm. glass helix packed column. To the residue was added 250 ml. of pentane. The salts that precipitated were collected by filtration and washed with pentane until the washings were colorless (ca. 500 ml.). The combined filtrate and washings were dried over magnesium sulfate and the pentane was removed by distillation through a 30-cm. column packed with glass helices. The residue was distilled through a 30-cm. Vigreux column to give 255 g. (67%) of IV, b.p. $111-116^\circ$ at 4.5 mm., lit.⁶ b.p. $128-130^\circ$ at 7 mm.

1,2,3,4,7,7-Hexachlorobicyclo[2.2.1]heptane-2 (V). **Method A.**—To 200 ml. of ethyl acetate and 0.3 g. of platinum dioxide was added 217 g. (0.73 mole) of diene IV. The mixture was reduced on a Parr hydrogenation apparatus until hydrogen uptake ceased (0.74 mole). The catalyst was removed by filtration and

the ethyl acetate was removed by distillation through a 30-cm. Vigreux column. The distillation was continued to give 175 g. (80%) of V, b.p. $112-116^\circ$ at 4.2 mm.

Method B.—Ethylene was bubbled for 24 hr. through 2538 g. (9.4 moles) of hexachlorocyclopentadiene that was maintained at 200° . The ethylene uptake was 244 g. Unreacted hexachlorocyclopentadiene was removed by distillation through a 90-cm. tantalum wire column, b.p. $123-135^\circ$ at 20 mm. Continued distillation at lower pressure gave 2630 g. (94%) of product V, b.p. 113° at 2-3 mm. The product solidified on standing, m.p. $37.5-39^\circ$, lit.⁸ b.p. 111° at 3 mm., m.p. 38° .

1,2,3,4-Tetrachlorobicyclo[2.2.1]heptene-2 (VII). **Method A.**—To an efficiently stirred solution of 203 g. (0.681 mole) of V in 1100 ml. of glacial acetic acid heated under reflux was added over 0.5-hr. period 250 g. (3.8 moles) of zinc dust (90% technical). The mixture was heated under reflux for an additional 8 hr., then cooled to room temperature. The unreacted zinc was removed by filtration through glass wool. The filtrate was poured into 2 l. of cold water, and the organic layer was extracted with a total of 900 ml. of pentane. The extract was washed successively with water, 10% sodium carbonate solution, and finally with water until the wash was neutral. The solution was dried over magnesium sulfate and the pentane was removed by distillation through a 30-cm. glass helix-packed column. The residue was distilled under nitrogen through a 90-cm. column packed with a stainless steel sponge. The first fraction gave 43.8 g. (29%) of compound VII, b.p. $74-77^\circ$ at 3 mm., which solidified on standing, m.p. $38-40^\circ$.

Anal. Calcd. for $C_7H_6Cl_4$: C, 36.24; H, 2.61; Cl, 61.15. Found: C, 36.49; H, 2.72; Cl, 61.10.

Later fractions contained compound VIII, which was isolated as described below. This reaction also was carried out several times at twice this scale with essentially identical yield.

Method B.—1,2,3,4-Tetrachlorocyclopentadiene (VI) was prepared by reduction of hexachloride II with zinc dust and acetic acid according to the procedure of Roedig.⁴ Ethylene was bubbled rapidly for 24 hr. through a solution of 40 g. (0.2 mole) of compound VI in 200 ml. of xylene. The reaction temperature was maintained at $120-125^\circ$ by an oil bath during the addition of ethylene. The xylene was removed by distillation at atmospheric pressure through a 90-cm. tantalum wire column. The residue was distilled to give 9 g. (20%) of compound VII, b.p. $70-72^\circ$ at 3 mm. The liquid distillate crystallized on seeding and cooling and melted at $37-38.5^\circ$ after crystallization from pentane and sublimation. The infrared spectrum of this sample was identical with the spectrum of compound VII prepared by method A above.

1,2,3,4,7-Pentachlorobicyclo[2.2.1]heptene-2 (VIII).—The distillation of the products of the reaction of zinc and acetic acid with V was usually discontinued after the tetrachloride VII had been collected. However, in one run with 100 g. of V, continued distillation gave 35 g. of XI (ca. 40%), b.p. $94-97^\circ$ at 3 mm., which solidified on standing. The solid had m.p. $59.2-59.8^\circ$ after three crystallizations from methanol.

Anal. Calcd. for $C_7H_5Cl_5$: C, 31.18; H, 1.89; Cl, 66.55. Found: C, 31.26; H, 1.89; Cl, 66.71.

1,4-Dichlorobicyclo[2.2.1]heptane (I).—A solution of 25 g. (0.11 mole) of compound VII and 17 g. (0.26 mole) of potassium hydroxide (85%) in 200 ml. of absolute methanol was shaken on a Parr hydrogenation apparatus at room temperature with 25 g. of Raney nickel. Hydrogen absorption was complete in less than 2 hr. The solution was filtered to remove the catalyst and then poured into 500 ml. of ice-water. The organic material was extracted three times with a total of 300 ml. of pentane and the combined extracts were dried over magnesium sulfate. Most of the solvent was removed by distillation through a 30-cm. column packed with glass helices. When the distillation flask was cooled the product separated as a solid, which was collected by filtration to give 15 g. (82%) of compound I, m.p. $78-79^\circ$. The solid was purified further by sublimation at 50° .

Anal. Calcd. for $C_7H_{10}Cl_2$: C, 50.95; H, 6.11; Cl, 42.96. Found: C, 50.90; H, 6.20; Cl, 42.90.

Conversion of I to Norbornane (X).—To a solution of 5 g. (0.03 mole) of compound I and 9.2 g. (0.12 mole) of *t*-butyl alcohol in 80 ml. of dry tetrahydrofuran was added 2 g. (0.28 g.-atom) of cut lithium ribbon. In 10-15 min., a vigorous exothermic reaction began and external cooling was necessary. After the initial reaction had subsided, the reaction mixture was heated under

reflux for 2 hr. It was then cooled, poured onto 1000 g. of ice, and extracted three times with a total of 200 ml. of pentane. The pentane solution was washed with water and dried over magnesium sulfate. The pentane was removed by distillation through a 30-cm. column packed with glass helices and the residue was analyzed by gas-liquid chromatography using a silicone oil on Chromosorb-P column. The retention time of the main peak (small solvent peaks were present also) was identical with that of an authentic norbornane sample. The infrared spectrum of a collected sample of the main peak was identical with the spectrum of norbornane.

Treatment of Compound I with Silver Nitrate.—A solution of compound XVI in saturated ethanolic silver nitrate was sealed in a test tube and heated at 100° for 30 hr. A shiny film formed on the walls of the tube dissolved completely on addition of 1:1 nitric acid and no nitric acid-insoluble material was formed in the reaction.

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Reactions of Enol Ethers with Carbenes. III.¹ Vinyl Sulfides and Δ^3 -Dihydrothiapyran²

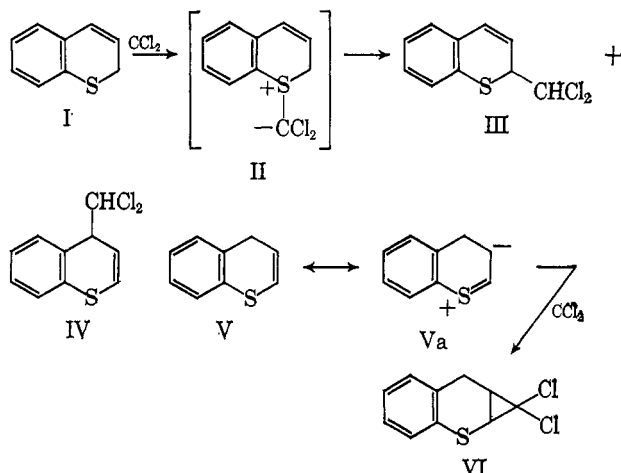
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The reactions of cyclic and noncyclic vinyl sulfides with ethyl trichloroacetate and sodium methoxide lead to the formation of cyclopropanes in high yields (60–77%). The reaction of cyclic allyl sulfides with these reagents leads to the formation of unsaturated insertion products.

In a previous study⁵ we observed that the reaction of 2H-1-benzothiapyran (I) with dichlorocarbene⁶ produced the insertion products III and IV, while reaction of the isomeric 4H-1-benzothiapyran (V), under identical conditions, produced only the cyclopropane VI.



The remarkable difference in behavior of these two isomeric olefins was attributed to the difference in nucleophilic character of the two double bonds (*i.e.*, V \leftrightarrow Va) relative to sulfur, and it was suggested that the reaction with I may involve the "ylid" intermediate II. Evidence was cited to indicate the carbanion derived directly from I or V was not an intermediate in either reaction.

(1) For the preceding article in this series, see W. E. Parham and M. O. Bhasvar, *J. Org. Chem.*, **29**, 1575 (1964).

(2) Supported in part by a grant (No. GP 159) from the National Science Foundation.

(3) In part from the Master's Thesis of L. Christensen, University of Minnesota, 1962.

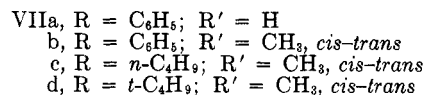
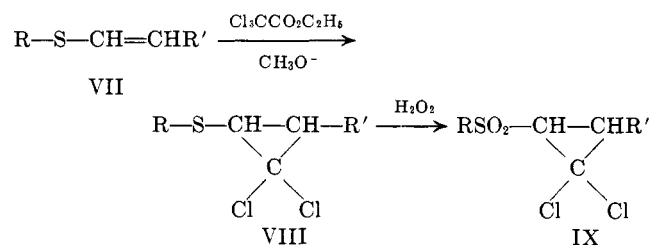
(4) In part from the dissertation of S. H. Groen, University of Groningen, The Netherlands. O.E.C.D. Postgraduate Travel Grant awarded by Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

(5) W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).

(6) The reaction was carried out with ethyl trichloroacetate and sodium methoxide and is assumed to involve formation of trichloromethyl anion, dichlorocarbene, and methyl ethyl carbonate. Cf. W. E. Parham and E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

In order to learn more about the generality and mechanism of these interesting transformations, an investigation of the reaction of saturated sulfides, and the reaction of α,β -, β,γ -, and γ,δ -unsaturated sulfides, with dichlorocarbene precursors was undertaken. This paper describes our preliminary findings with vinyl sulfides and the isomeric Δ^2 - and Δ^3 -dihydrothiapyrans.

The reactions of the α,β -unsaturated sulfides VIIa–d (1 mole) with ethyl trichloroacetate (1.1–1.6 moles)



and sodium methoxide (1.3–2.0 moles) was carried out in olefin-free petroleum ether (b.p. 30–60°) using conditions previously described for other olefins.⁶ In each case high yields of the corresponding cyclopropanes VIII (60–77%) were obtained.⁷ The dichlorocyclopropanes were characterized by their composition and spectra (infrared, ultraviolet, and n.m.r., see Experimental), and by conversion to the corresponding sulfones IX. The olefins VIIb–d were mixtures of *cis* and *trans* isomers, prepared by isomerization⁸ of the corresponding allyl sulfides; the corresponding cyclopropanes VIIIb–d were, as expected, mixtures of *cis* and *trans* isomers (by n.m.r. and v.p.c.).

(7) Subsequent to the completion of our work E. P. Prilezhaeva, N. P. Petukhova, and M. F. Shostakovskii [*Dokl. Akad. Nauk SSSR*, **144**, 1059 (1962); *Chem. Abstr.*, **57**, 13,632 (1962)] described the preparation of the 1,1-dichlorocyclopropanes from ethyl vinyl sulfide and phenyl vinyl sulfide in 40 and 25.9% yield, respectively, by reaction with chloroform and potassium *t*-butylate. These authors also describe the sulfoxide and sulfone derivatives of the cyclopropyl adducts.

(8) D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).