# Addition of Dihalocarbenes to Cyclic Dienes

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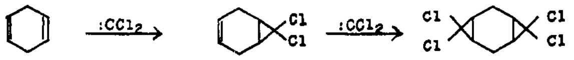
THIRTEEN new bicyclic and tricyclic halogenated hydrocarbons and their derivatives, containing the elements of dichlorocarbene or dibromocarbene, have been prepared as a part of a program to develop new industrial organic chemicals (Table I).

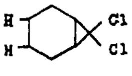
1,4-Cyclohexadiene reacted with dichlorocarbene generated by the method of Parham and Schweizer (*12*) to yield 7,7-dichloro-3-bicyclo[4,1,0]heptene, I, as the major component and a high melting solid, presumably 4,4,8,8-tetrachloro-tricyclo$[5,1,0,0^{3,5}]$octane, II, arising by further interaction of I with dichlorocarbene. The tricyclic derivative II is analogous to the products obtained recently from methylene (*10*) and from dibromocarbene (*8*). Moreover, structure II was confirmed by the facile conversion of I to II in the presence of additional dichlorocarbene.



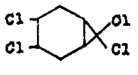
I II

7,7-Dichloro-3-bicyclo[4,1,0]heptene was identified through its infrared spectrum, elemental analysis, and hydrogenation to the known 7,7-dichloro-bicyclo[4,1,0]-heptane, III (*4*). The olefin I added one mole of bromine or of chlorine readily to yield the corresponding tetrahalo derivatives IV, IVa.

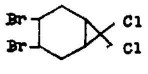
1,4-Cyclohexadiene reacted with dibromocarbene generated from bromoform and commercial potassium *tertiary*-butoxide (*11*) to give the mono-adduct 7,7-dibromo-3-bicyclo[4,1,0]heptene, V, and the di-adduct 4,4,8,8-tetrabromo-tricyclo$[5,1,0,0^{3,5}]$octane, VI (*8, 14*).



III

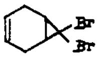


IV

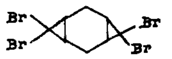


IVa

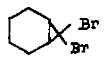
The olefin was identified through its physical properties, infrared spectrum, elemental analysis, and catalytic hydrogenation to the known 7,7-dibromobicyclo[4,1,0]heptane, VII (*3, 4*). It was converted to the tricyclic derivative VI in the presence of additional dibromocarbene.



V



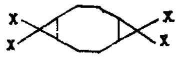
VI



VII

1,5-Cyclo-octadiene (*1*) reacted with dihalocarbenes in a manner similar to that of 1,4-cyclohexadiene, to yield the corresponding 9,9-dihalo-4-bicyclo[6,1,0]nonenes VIII and VIIIa, and the 5,5,10,10-tetrahalo-tricyclo$[7,1,0,0^{4,6}]$ decanes IX and IXa. The compounds VIII and VIIIa were identified by catalytic hydrogenation to the corresponding bicyclononanes X and Xa (*6*), which were also prepared from cyclo-octene and the requisite dihalocarbene.

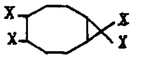
VIII, X = Cl
VIIIa, X = Br



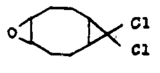
IX, X = Cl
IXa, X = Br

X, X = Cl
Xa, X = Br

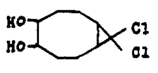
9,9-Dichloro-4-bicyclo[6,1,0]nonene, VIII, was converted to the dichloro, dibromo, epoxy, and dihydroxy derivatives XI-XIII by known methods.



XI, X = Cl
XIa, X = Br



XII



XIII

## EXPERIMENTAL PROCEDURE

**7,7-Dichloro-3-Bicyclo[4,1,0]heptene.** Ethyl trichloroacetate, 191 grams, was added with rapid stirring to a suspension of 75 grams sodium methoxide in 500 ml. pentane and 40 grams 1,4-cyclohexadiene in 30 minutes while the reaction mixture was amintained at 0°-5° C. The mixture was stirred at 0°-5° C. for 6 hours.

After standing overnight the reaction mixture was transferred to a separatory funnel containing 500 ml. water, the organic layer was separated, washed with two 250 ml. portions of water, dried over sodium sulfate and concentrated to 100 ml. on a steam bath. The concentrate was cooled to −20° C. when crystals of 4,4,8,8-tetrachlorotricyclo$[5,1,0,0^{3,6}]$octane separated. After two crystallizations from carbon tetrachloride it melted at 182°-3° C.

The solution of 7,7-dichloro-3-bicyclo[4,1,0]heptene in pentane was fractionated to give 36.8 grams of product boiling at 82°-4° C. and 12 mm.

4,4,8,8-Tetrachlorotricyclo$[5,1,0,0^{3,5}]$octane, 9,9-dichloro-4-bicyclo[6,1,0]nonene, 5,5,10,10-tetrachlorotricyclo$[7,1,0,0^{4,6}]$decane, 7,7-dichlorobicyclo[4,1,0]heptane, and 9,9-dichlorobicyclo[6,1,0]nonane were similar prepared by the reaction of dichlorocarbene with the appropriate olefin.

**9,9-Dibromo-4-Bicyclo[6,1,0]nonene.** A solution of 253 grams of bromoform in 250 ml. pentane was added to a suspension of 112 gram of potassium tertiary-butoxide in 108 grams of 1.5-cyclooctadiene and 500 ml. of pentane with rapid stirring at 0°-5° C. The reaction mixture was then stirred at 0° C. for 6 hours then allowed to stand overnight. It was then transferred to a separatory funnel containing 1 liter of water, the organic layer was separated, washed with two 250 ml. portions of water and dried over sodium sulfate. The solvent was evaporated on a steam bath and the residue cooled to −20° C. to precipitate 20 grams of 5,5,10,10-tetrabromotricyclo$[7,1,0,0^{4,6}]$decane melting at 173°-4° C., after two recrystallizations from carbon tetrachloride.

The filtrate was distilled to give 163 grams of 9,9-dibromo-4-bicyclo[6,1,0]nonene boiling at 136°-7° C. and 12 mm.

7,7-Dibromo-3-bicyclo[4,1,0]heptene, 4,4,8,8-tetrabromo-tricyclo$[5,1,0,0^{3,6}]$octane, 7,7-dibormobicyclo[4,1,0]heptane and 9,9-dibromobicyclo[6,1,0]nonane were prepared in an analogous manner.

**Catalytic Hydrogenation of 9,9-Dichloro-4-bicyclo[6,1,0]-nonene.** A solution of 27.1 grams of 9,9-dichloro-4-bicyclo-[6,1,0]nonene in 200 ml. absolute alcohol and 0.10 grams of platinum oxide catalyst was treated with hydrogen at a pressure of 40-5 p.s.i. until no further hydrogen uptake

Table I. Physical Properties of Bicyclic and Tricyclic Compounds Prepared

| | | | Analysis | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calcd., % | | | | Found, % | | | | |
| Structure | Yield, % | B.P., ° C. (M.P., ° C.) | C | H | Cl | Br | C | H | Cl | R | |
| I | 45 | 82–84 at 12 mm. | 51.53 | 4.92 | 43.55 | | 51.32 | 4.11 | 43.28 | | |
| II | 42 | (182–183) | 39.03 | 3.25 | 57.72 | | 38.79 | 3.58 | 57.81 | | |
| III | 78 | 82–84 at 16 mm. | | | | | | | | | (*3, 4, 7, 9, 12*) |
| IV | 75 | (52–53) | 35.90 | 3.42 | 60.68 | | 36.10 | 3.44 | 60.57 | | |
| IVa | 72 | (94–95) | 26.04 | 2.50 | 21.96 | 49.50 | 26.03 | 2.84 | 21.76 | 49.71 | |
| V | 37 | 110–112 at 16 mm. | 33.36 | 3.20 | ... | 63.44 | 33.24 | 3.18 | ... | 62.98 | (*8, 14*) |
| VI | 47 | (36–37)<br>(213–214) | 22.67 | 1.90 | ... | 75.42 | 22.64 | 1.88 | ... | 75.41 | (*8, 14*) |
| VII | 64 | 108–110 at 12 mm. | ... | ... | ... | 63.0 | ... | ... | ... | 63.1 | (*3, 4, 13*) |
| VIII | 62 | 115–116 at 12 mm. | 56.54 | 6.28 | 37.18 | ... | 56.38 | 6.42 | 36.69 | ... | |
| VIIIa | 58 | 136–137 at 12 mm. | 38.60 | 4.32 | ... | 57.08 | 38.41 | 4.37 | ... | 57.26 | |
| IX | 73 | (185–186) | 43.80 | 4.38 | 51.82 | ... | 43.77 | 4.64 | 52.01 | ... | |
| IXa | 44 | (173–174) | 26.59 | 2.65 | ... | 70.75 | 26.82 | 2.35 | ... | 71.04 | |
| X | 78 | 114–116 at 12 mm. | 55.96 | 7.26 | 36.78 | ... | 56.04 | 7.02 | 36.61 | ... | |
| Xa | 60 | 144–145 at 16 mm. | | | | | | | | | (*6*) |
| XI | 68 | (53–54) | 41.25 | 4.51 | 54.24 | ... | 41.21 | 4.57 | 54.12 | ... | |
| XI*a* | 74 | (64–65) | 30.80 | 3.45 | 20.21 | 45.55 | 30.46 | 3.23 | 20.32 | 45.60 | |
| XII | 64 | 138–139 at 7 mm. | 52.20 | 5.84 | 34.24 | ... | 52.08 | 5.53 | 34.32 | ... | |
| XIII | 38 | Oil | 48.02 | 6.27 | 31.50 | ... | 47.64 | 6.42 | 31.21 | ... | |

occurred. The reaction mixture was filtered and fractionated to yield 24 grams of product boiling 115°–16° C. at 14 mm. and possessing an infrared spectrum identical to that of 9,9-dichlorobicyclo[6,1,0]nonane obtained by the addition of dichlorocarbene to cyclooctene.

7,7-Dichloro-3-bicyclo[4,1,0]heptene, 7,7-dibromo-3-bicyclo[9,1,0]heptene, and 9,9-dibromo-4-bicyclo[6,1,0]-nonene were similarly reduced to the corresponding saturated bicyclic halocarbons which were also prepared by the addition of dichloro- or dibromocarbene to the appropriate olefin. In all cases infrared spectra were compared and proved identical.

**Epoxidation of 9,9-Dichloro-4-bicyclo[6,1,0]nonene.** Twenty-seven grams of VIII and 2.0 grams of anhydrous sodium acetate were cooled to 20° C. and 30 grams of 40% commercial peracetic acid was added dropwise, with stirring, in ½ hour at 20–5° C. The mixture was stirred 1 hour, heated 1 hour on a steam bath, transferred to a separatory funnel containing 100 ml. of cold water, the epoxide removed, dried over calcium chloride, and distilled. The product, 5-oxa-10,10-dichlorotricyclo[7,1,0,$0^{4,6}$]decane, boiled at 136°–7° C. and 7 mm., and showed a strong absorption band at 8.1 $\mu$ in its infrared spectrum for the epoxy group (*8*).

**4,5-Dihydroxy-9,9-dichlorobicyclo[6,1,0]nonane.** Twenty-seven grams of 9,9-dichloro-4-bicyclo[6,1,0]nonene in 100 ml. 90% formic acid was treated with 18 grams of 30% hydrogen peroxide at 50°–60° C. in 2 hours. The reaction mixture was diluted with 100 ml. of water to precipitate the diol and unreacted olefin. The organic layer was dried over anhydrous magnesium sulfate, decolorized with alumina and evacuated at 120° C. and 2 mm. pressure to remove volatile components. A clear viscous product remained which showed a strong absorption band at 2.75 microns for the 1,2-diol system (*2*).

**Bromination of 7,7-Dichloro-3-bicyclo[4,1,0]heptane.** A solution of 18 grams of bromine in 100 ml. of carbon tetrachloride was added to 16.3 grams of the olefin and 100 ml. of carbon tetrachloride. The mixture was allowed to stand at 0° C. overnight, washed with 5% sodium carbonate solution, dried over sodium sulfate and concentrated on a steam bath to 50 ml. The concentrate was cooled to −20° C. to precipitate 3,4-dibromo-7,7-dichlorobicyclo[4,1,0]heptane melting at 94°–5° C. after recrystallization from carbon tetrachloride.

3,4,7,7-Tetrachlorobicyclo[4,1,0]heptane, 4,5-dichlorobicyclo[6,1,0]nonane and 4,5-dibromobicyclo[6,1,0]nonane were prepared by the same method.

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