

## Some Halogen Derivatives of Cyclohexane

O. HASSEL and K. LUNDE

*Universitetets Kjemiske Institutt, Blindern — Oslo, Norway*

The general knowledge about the chemistry of even the simplest derivatives of *cyclohexane* is still rather incomplete and the number of substances accessible for molecular structure analysis comparatively small. Before this part of chemistry has been more thoroughly investigated, workers interested in the stereochemistry of six-membered rings will have to carry out a great deal of preparative work in order to supply compounds suited for molecular structure determinations.

We have considered halogen derivatives of *cyclohexane* especially well suited for such determinations, and in the course of our structural investigations some preparative work dealing with those substances has therefore been carried out which has so far not been published. In most cases we had only comparatively small quantities of substance at our disposal and we therefore limited our work to crystalline substances the purity of which is more easily stated than in the case of liquids.

### DI- AND TRIHALOGEN DERIVATIVES

We first bring some observations related to disubstituted *cyclohexanes*: The lower melting dibromo- and diiodo-*cyclohexanes* obtained besides the *trans* 1,4-compounds when resorcitol or chinitol is treated with strong hydrobromic resp. hydroiodic acid should be expected to be corresponding compounds and perhaps isomorphous. The bromo-compound does not appear to be easily obtained in a pure state, and the melting points recorded by different authors differ appreciably. The highest figure earlier reported is 48° C<sup>1</sup>, but we observed a melting point of 51° C using single crystals. The crystals are monoclinic and the unit cell indicates a close crystallographic relationship between this compound and the 1,4(*trans*) compound, a rather surprising result which is being further investigated in our laboratory. The diiodo-compound

turned out to be triclinic and not isomorphous with the dibromo-compound. At a temperature not far from the melting point earlier reported <sup>2</sup> (67.5° C), however, it undergoes a transition into a new modification which may perhaps be monoclinic and correspond to that of the dibromocompound. The melting point of this modification is 84° C. It may be cooled and kept below the transition temperature for some time without suffering transition into the modification stable at room temperature.

Some experiments were performed in order to prepare 1,3,5-trihalogen-*cyclohexanes* treating  $\alpha$  or  $\beta$  phloroglucitol with strong hydrochloric and hydrobromic acid or in some cases with other reactants usually employed in order to replace hydroxy groups by halogens. These attempts were unsuccessful; when hydrochloric or hydrobromic acid was used the formation of benzene could be observed. It would seem that the 1,3,5-trihalogen compounds are unstable at higher temperatures.

#### 1,2,3,4,-TETRAHALOGEN DERIVATIVES

Of the six possible substances containing four bromine atoms (Fig. 1) *two* have been known with certainty for a couple of years, having the melting points 156° and 90° respectively <sup>3</sup>. The existence of a third substance melting at 141° <sup>4</sup> has been questioned <sup>3</sup>. Our investigation clearly proves that this substance really does exist. According to the crystal structure determination carried out in our laboratory by Wang Lund <sup>5</sup>, this substance has the configuration  $\kappa \kappa \kappa \kappa$  (Fig. 1 a). The unit cells and space groups of the higher and the lower melting substances have also been reported in Wang Lunds paper. Unfortunately the crystal structure determination is more involved in these cases. With the aim of facilitating the structure determination we have prepared a dichlorodibromocompound from 1,3-*cyclohexadiene* by first adding two atoms of chlorine and subsequently two atoms of bromine. This compound melting at 128° C would be expected to be a 1,4-dichloro-2,3-dibromo-*cyclohexane* and as a matter of fact it turned out to be isomorphous with the 1,2,3,4-tetrabromocompound of m. p. 156° C:

	a (Å)	b (Å)	c (Å)	$\beta$	Space group
1,2,3,4-tetrabromocyclohexane	9.91	8.52	8.06	133°	P 2 <sub>1</sub>
1,4-dichloro-2,3-dibromocyclohexane	9.58	8.31	7.32	129°	P 2 <sub>1</sub>

An attempt to prepare 1,4-dibromo-2,3-dichlorocyclohexane by adding two atoms of chlorine to 1,4-dibromocyclohexene(2) was unsuccessful. Bromine was liberated and chlorine substitution products formed, among them  $\beta$  benzene hexachloride.

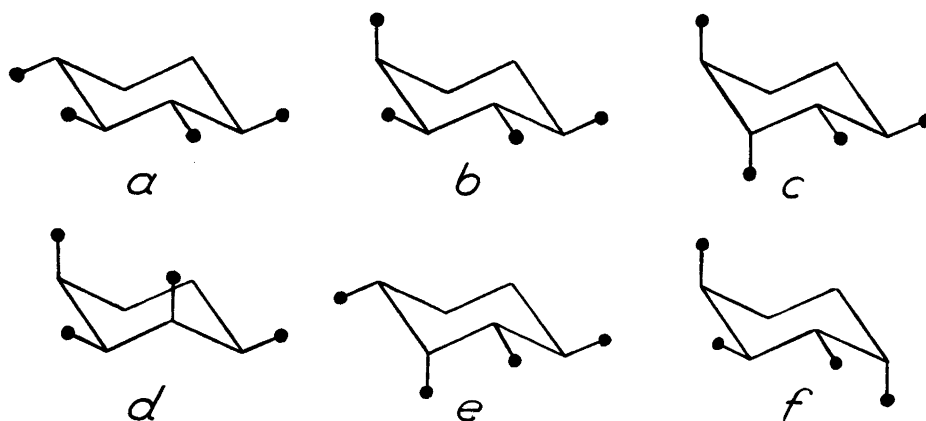


Fig. 1. Possible configurations of 1,2,3,4-tetrabromocyclohexanes. *a, b, e, f* may exist in independent mirror image forms; the enantiomorphous forms of *c* and *d* are transformed into each other by a "conversion" of the carbon ring.

If a stream of chlorine is led into 1,3-cyclohexadiene both addition to the double bonds and substitution takes place, and considerable quantities of  $\alpha$  benzene hexachloride are formed. From the reaction product obtained by adding the theoretical amount of chlorine to the diene, however, two different tetrachlorocyclohexanes could be isolated, one melting at  $112^\circ\text{C}$ , the other at  $116^\circ$ . Both compounds would be expected to be 1,2,3,4-tetrachlorocyclohexanes. We have not, however, been able to find any indication of isomorphism between at least the lower melting isomer and any of the 1,2,3,4-tetrahalogenocyclohexanes mentioned above.

The fact that we have been able to prepare *three* different 1,2,3,4-tetrabromocyclohexanes by adding two atoms of bromine to the pure 1,4-dibromocyclohexene(2) of m. p.  $108^\circ$  clearly demonstrates that caution is needed when drawing conclusions about the steric course of addition processes. If we assume that only *trans* addition to the double bond takes place, it would not be possible to obtain more than *two* different 1,2,3,4-tetrabromocyclohexanes starting with one of the two possible forms of 1,4-dibromocyclohexene(2). It has to be borne in mind, however, that the actual reaction scheme may include either an isomeric change from 1,4-dibromocyclohexene(2) into 1,2-dibromocyclohexene(3) or a partial *cis-trans* transition of the 1,4-dibromocyclohexene(2).

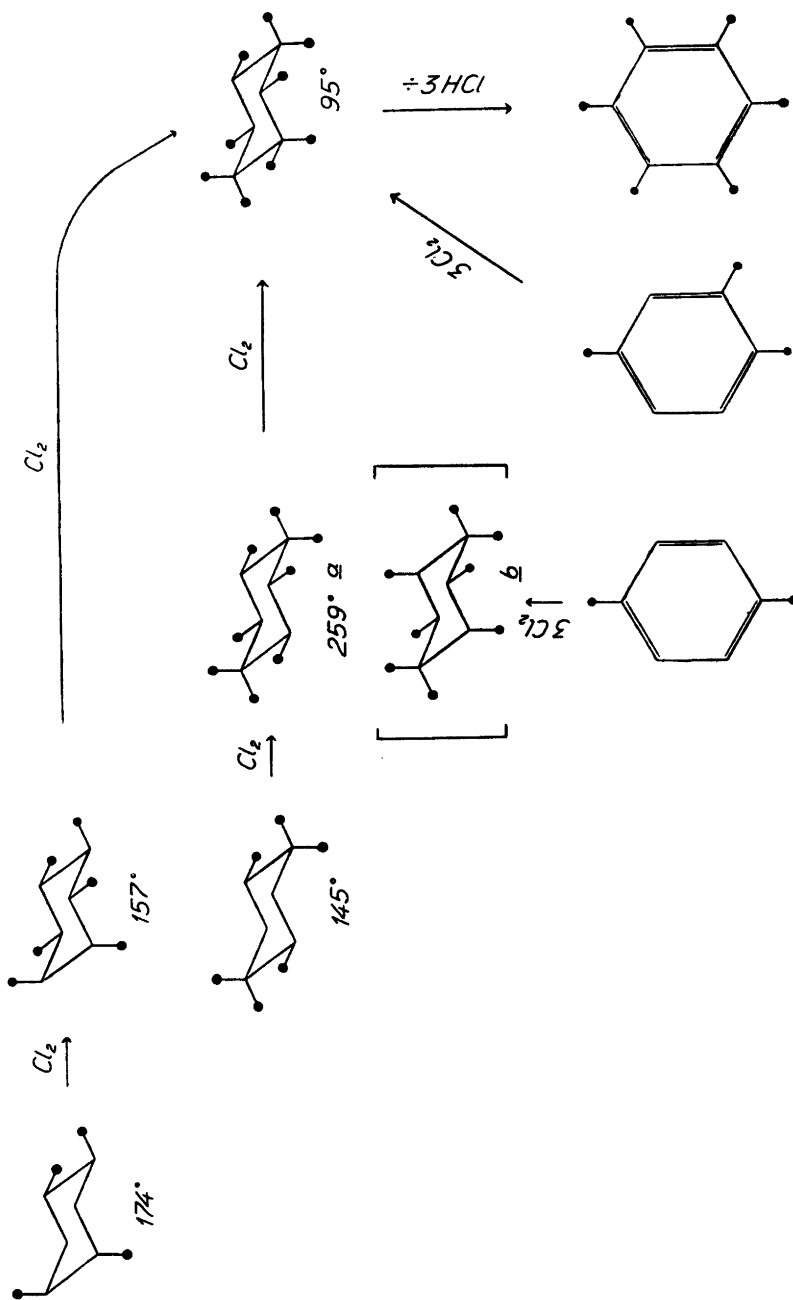


Fig. 2. The mutual relationship between some chlorinated cyclohexanes and the connection between some of these substances and chloroderivatives of benzene.

## CHLORINATION PRODUCTS OF CYCLOHEXANE

Many experiments have already been carried out on the chlorination of *cyclohexane*, and a number of new substances has thus been obtained. In most cases, however, the positions of the chlorine atoms have not been stated and very little is also known about the mutual relationship between the compounds successively formed during the chlorination. Systematic work dealing with the continued chlorination of intermediate products isolated in a pure state would no doubt be of great value in determining the real structure of higher chlorinated compounds.

The simplest assumption to be made when discussing the structural relationship of the chlorination products successively formed, is that bonds between carbon and chlorine already existing are not broken during the chlorination processes.

In the course of a chlorination continued until further absorption of chlorine could hardly be detected the following substances were isolated in a pure state: tetrachlorocyclohexane (m. p. 174°),  $\alpha$  benzene hexachloride (157°), hexachlorocyclohexane (145°), hexachlorobenzene (227°), octachlorocyclohexane (259°) and nonachlorocyclohexane (95°).

Here the  $\alpha$  benzene hexachloride is probably formed from the tetrachlorocyclohexane of m. p. 174°, the former having the configuration  $1\epsilon\ 2\epsilon\ 3\kappa\ 4\kappa\ 5\kappa\ 6\kappa$  (Fig. 2, (6)—157°) and the latter the configuration  $1\epsilon\ 2\epsilon\ 4\kappa\ 5\kappa$  (Fig. 2, (4)—174°). As a matter of fact we have detected  $\alpha$  benzene hexachloride in the chlorination product of pure tetrachlorocyclohexane (174°).

It has already been pointed out that the hexachlorocyclohexane of m. p. 145° cannot be a benzene hexachloride<sup>7</sup>. Recently results of X-ray analysis and electron diffraction work has shown this substance to have the configuration  $1(\kappa\epsilon)\ 2\kappa\ 4(\kappa\epsilon)\ 5\kappa$  (Fig. 2, (6)—145°). The octachloro compound of m. p. 259°, according to (unpublished) results obtained by E. Wang Lund, has zero dipole moment, and the X-ray analysis requires centrosymmetric molecules to be present in the crystals. By the kindness of this investigator we are able to report the crystallographical data of the substance:

$$a = 8.05 \text{ \AA}, b = 11.01 \text{ \AA}, c = 6.74 \text{ \AA}, \beta = 108.5^\circ \quad \begin{array}{l} \text{Space group} \\ P2_1/a \end{array}$$

The density is 2.06, and the unit cell therefore contains *two* molecules. This octachloro-compound is identical with the substance obtained by addition of chlorine to *p*-dichlorobenzene. Therefore, only *two* possible configurations of this substance should have to be considered a)  $1(\kappa\epsilon)\ 2\kappa\ 3\kappa\ 4(\kappa\epsilon)\ 5\kappa\ 6\kappa$  and

b) 1( $\kappa\epsilon$ ) 2 $\epsilon$  3 $\kappa$  4( $\kappa\epsilon$ ) 5 $\epsilon$  6 $\kappa$  (Fig. 2 (8)—259°). The complete structure analysis has not yet been finished, but configuration *a* must no doubt be regarded more probable than *b*. We have indeed found that the octachloro*cyclohexane* (259°) may be obtained if the hexachloro-compound (145°) is chlorinated using the amount of chlorine theoretically necessary to form an octachloro*cyclohexane*. The nonachloro*cyclohexane* (95°), however, is the main product even under these circumstances.

This nonachloro-compound (95°) is probably identical with the compound earlier obtained<sup>9</sup> by treating 1,2,4-trichlorobenzene with chlorine. We have obtained this substance both from *p*-dichlorobenzene and chlorine and by chlorination of octachloro*cyclohexane* (259°). It is somewhat surprising, however, that the chlorination of the octachloro*cyclohexane* into nonachloro*cyclohexane* appears to proceed very slowly, as during the chlorination of the hexachloro*cyclohexane* (145°) into the nonachloro-compounds we would expect the octachloro*cyclohexane* (259°) to represent an intermediate stage. If the octachloro*cyclohexane* (259°) is assumed to have the configuration *a* (see above) the nonachloro*cyclohexane* must have the configuration 1( $\kappa\epsilon$ ) 2( $\kappa\epsilon$ ) 3 $\kappa$  4( $\kappa\epsilon$ ) 5 $\kappa$  6 $\kappa$  (Fig. 2 (9)—95°).

The presence of hexachlorobenzene in the distillation product of chlorinated *cyclohexane* mentioned above is no doubt due to thermal decomposition of the nona-compound present in the chlorination mixture. We have indeed observed that the distillation *in vacuo* of pure nona-compound results in the partial formation of hexachlorobenzene, another part of the nona-compound distilling without decomposition.

The structure (Fig. 2 (9)—95°) attributed to the nona-compound is in good agreement with the observation that this compound is obtained by chlorination of tetrachloro*cyclohexane* (174°), of  $\alpha$  benzene hexachloride, of hexachloro*cyclohexane* (145°) and of octachloro*cyclohexane* (259°). This view is supported by the observation made by Oiwa and coworkers<sup>10</sup> who obtained the nona-compound also by chlorinating  $\beta$ ,  $\delta$  and  $\epsilon$  benzene hexachlorides and finally by chlorination of octachloro*cyclohexane* of m. p. 149°. This octa-compound is obtained by addition of chlorine to *o*-dichlorobenzene and the authors assume it to have the configuration 1( $\kappa\epsilon$ ) 2( $\kappa\epsilon$ ) 3 $\kappa$  4 $\kappa$  5 $\kappa$  6 $\kappa$ .

As the nona-compound of m. p. 95° is the end product of chlorination of a number of different chlorinated *cyclohexanes* it seemed of interest to establish its crystallographic data in order to make its identification quite unambiguous. E. Wang Lund has kindly placed his results at our disposal. The crystals are monoclinic with 4 molecules in the unit cell. The monoclinic angle is 109.7° and the lattice constants are  $a = 8.54 \text{ \AA}$ ,  $b = 26.3 \text{ \AA}$ ,  $c = 5.87 \text{ \AA}$  (density calc. 2.12).

## EXPERIMENTAL

Reaction of phloroglucitol with hydrochloric  
(hydrobromic) acid

5 g  $\alpha$  or  $\beta$  phloroglucitol were heated to 100–120° in sealed tubes with an excess of concentrated acids (saturated at 0° C). The upper layer formed during the reaction was isolated, washed with a solution of sodium bicarbonate and with pure water, dried and distilled. The liquid boiling at 80–81° C had the odour of benzene and was identified as such by nitration into dinitrobenzene. Neither  $\alpha$  nor  $\beta$  phloroglucitol seem to react with  $\text{PCl}_5$  in benzene solution, with  $\text{PCl}_3$  or  $\text{POCl}_3$ .

## 1,2,3,4-Tetrabromocyclohexanes

The cyclohexadiene used in preparing 1,2,3,4-tetrahalogen-compounds was prepared according to Crossley<sup>11</sup>. 0.2 moles of the diene were dissolved in 100 ml chloroform and 0.4 moles of bromine added drop by drop under stirring. The first 0.2 moles of bromine are immediately absorbed. The remaining part within two or three days when the reaction mixture is kept in a dark and cool place. The solvent is evaporated *in vacuo*, a possible small excess of bromine being simultaneously removed during this process. After being kept at 0° C for a few days the remaining oily substance crystallizes partially. After two recrystallizations from small amounts of ethyl ether the solid consists chiefly of large compact crystals, but partially also of thin needles. A preliminary separation of the two sorts of crystals could easily be performed by hand. After recrystallization of the former crystals from ethyl ether, well developed polyhedrons of m. p. 89–90° C were obtained:

$(\text{C}_6\text{H}_8\text{Br}_4)$	Calc.	Br	80.00
	Found	»	80.35

The thin needles were recrystallized from methanol until the m. p. was constant — 156° C. Having only a limited quantity of substance at our disposal the analysis was performed on a sample containing a mixture of the two isomers and melting from 135–142°:

$(\text{C}_6\text{H}_8\text{Br}_4)$	Calc.	Br	80.00
	Found	»	80.01

We have also prepared the two tetrabromocyclohexanes just mentioned by adding one mole of bromine to 1,4-dibromocyclohexene(2) in  $\text{CCl}_4$  solution. In this case the raw product was first recrystallized from methanol. Beside the needle-shaped crystals of the higher melting isomer the first fraction also contained very thin crystal plates of a substance melting at 140°. This third isomer could be prepared in a pure state by adding less than 0.2 moles of bromine to 0.1 moles of diene dissolved in 100 ml of carbon tetrachloride. After being kept for a couple of days in the dark at room temperature the solution was colourless and a white, crystalline precipitate was formed. By recrystallization from ligroin fibre-like crystals melting at 142° were obtained. The crystals obtained from ethyl ether were well developed pyramids:

$(\text{C}_6\text{H}_8\text{Br}_4)$	Calc.	Br	80.00
	Found	»	80.37

## Dichloro-dibromocyclohexane

A solution of 0.1 moles of chlorine in carbon tetrachloride is added to a cooled solution of 0.1 moles of diene in the same solvent. Subsequently a solution of 0.1 moles of bromine in carbon tetrachloride is added and the solution is kept in the dark for two or three days. After evaporation of the solvent from the (colourless) solution an oily substance is obtained which crystallizes partially after being kept at 0° C for some time. After recrystallization from ligroin needle-shaped crystals are obtained melting at 128° C:

(C <sub>6</sub> H <sub>8</sub> Br <sub>2</sub> Cl <sub>2</sub> )	Calc.	Mol.wt.	311	Cl	22.81	Br	51.40
	Found	»	»	305	»	22.68	»

0.1 moles of chlorine were added to 0.1 moles 1,4-dibromocyclohexene(2) in carbon tetrachloride solution. When the solution is kept in the dark for a couple of days bromine is liberated. After evaporation *in vacuo* the oily substance left is cooled and then deposits crystals which after recrystallization from benzene have a melting point of 308° C and which could be identified as β benzene hexachloride.

## Tetrachlorocyclohexanes

When a stream of chlorine is led into a solution of the diene without taking special precautions, both addition of chlorine and substitution takes place even in the dark, and higher chlorinated products, among them α benzene hexachloride, are formed. If, however, working in the dark and at -10° C, a solution of 0.2 moles of chlorine in carbon tetrachloride is added to a solution of 0.1 moles of diene, and the mixture kept at 0° C for some days, the oily product obtained after evaporation of the solvent deposits crystals of a new kind. If the remaining oil is distilled *in vacuo* additional crystals are obtained from the fraction boiling between 120 and 125° (12 mm). After recrystallization from ethyl ether needle-shaped crystals of m. p. 112° are obtained:

(C <sub>6</sub> H <sub>8</sub> Cl <sub>4</sub> )	Calc.	Cl	63.91
	Found	»	63.51

Once, however, under similar conditions, a different tetrachlorocompound crystallizing in extremely thin needles was obtained having a melting point of 116° C:

(C <sub>6</sub> H <sub>8</sub> Cl <sub>4</sub> )	Calc.	Cl	63.91
	Found	»	63.68

## Chlorination products of cyclohexane

On chlorinating cyclohexane or monochloro-cyclohexane in artificial light a deposit of tetrachlorocyclohexane (m. p. 174° C) is formed. Additional quantities may be obtained from the first fraction of the remaining liquid boiling between 110° and 130° C (10 mm). When a solution of this tetrachlorocompound, recrystallized from carbon tetrachloride and again dissolved in the same solvent, is treated with chlorine using artificial light, the end product of the chlorination is nonachlorocyclohexane of m. p. 95° C. If the chlorination is interrupted after 15 minutes and the solvent, the excess of chlorine and the hydrogen chloride removed *in vacuo*, an oily substance remains, a fraction of which, boiling at



150—160° (10 mm) and kept for some time at 0° C, deposits crystals which could be identified as  $\alpha$  benzene hexachloride.

$\alpha$  benzene hexachloride may also be isolated from the fraction boiling at 150—160° (10 mm) after removing the solid tetrachlorocompound from the product obtained by direct chlorination of *cyclohexane*. From the same fraction hexachloro*cyclohexane* of m. p. 145° is also deposited if it is kept at a low temperature for some time.

The direct chlorination of a solution of the 145° substance in carbon tetrachloride leads to nonachloro*cyclohexane* of m. p. 95° C, which is identical with the substance obtained from tetrachloro*cyclohexane* of m. p. 174° (see above) and the nonachloro-*cyclohexane* which we obtained on leading a stream of chlorine into a solution of *p*-dichlorobenzene in  $\text{CCl}_4$  using artificial light. The chief product in the last mentioned experiment is octachloro*cyclohexane* of m. p. 259° C (“ $\beta$ -*p*-dichlorobenzene hexachloride”). If, however, the chlorination of the 145° substance is performed by adding a solution of 1.2 g chlorine in carbon tetrachloride to a solution containing 5 g of the substance and this mixture exposed to artificial light for 24 hours, octachloro*cyclohexane* of m. p. 259° is obtained beside the nonachloro*cyclohexane*.

Returning to the direct chlorination of *cyclohexane* it may be stated that the fraction of the chlorinated product distilling at 160—175° deposits very thin needles melting at 226° which are identified as hexachlorobenzene. After some time the mother liquid yielded new crystals which could be identified as nonachloro*cyclohexane* of m. p. 95°. If heated, this compound begins to split off hydrogen chloride at about 160° C. If the temperature is maintained at 200° C for some time this reaction is nearly complete and the nonachloro*cyclohexane* is transformed into hexachlorobenzene. A distillation carried out at a pressure of about 10—12 mm transforms about 30 % of the nonacomound into hexachlorobenzene, the rest distilling unchanged.

The fraction boiling between 175° and 185° deposits crystals of the octachloro*cyclohexane* of m. p. 259°. This substance, after being dissolved in carbon tetrachloride, was chlorinated for 24 hours in artificial light. After the solvent had been evaporated the greater part of the octachloro-compound is deposited unchanged, but an oily rest is left which subsequently deposits crystals of nonachloro*cyclohexane* of m. p. 95°.

#### SUMMARY

Some observations regarding the lower melting dibromo- and diiodo*cyclohexanes* obtained from 1,4- and 1,3-*cyclohexandiols* and concentrated hydrogen-halogen acids are reported. Attempts to prepare 1,3,5-trihalogen-*cyclohexanes* from phloroglucitol and hydrochloric or hydrobromic acids were unsuccessful and led to the formation of benzene.

It could be proved that the tetrabromo*cyclohexane* of m. p. 145° obtained from 1,3-*cyclohexadiene* and bromine is a well-defined chemical individual. A complete crystal structure determination by E. Wang Lund has proved that the bromine atoms occupy the positions: 1 $\kappa$  2 $\kappa$  3 $\kappa$  4 $\kappa$ . A dichlorodibromo-*cyclohexane* of m. p. 128° has been prepared which is isomorphous with the tetrabromocompound of m. p. 156°. Two new tetrachloro*cyclohexanes*, melting at 112° and 116° respectively, have been prepared from 1,3-diene and chlorine.

Experiments in which *cyclohexane* was chlorinated in artificial light are described. In one fraction of the distillation product hexachlorobenzene was observed. This substance is formed from nonachloro-*cyclohexane* (m. p. 95°) by thermal decomposition. It is found that the configurations now attributed to the different chlorination products successively formed by substituting hydrogen by chlorine agree with those to be expected if we assume that carbon-chlorine bonds already established are not broken in the course of further substitution reactions.

## REFERENCES

1. Zelinsky, N. D., and Kozeschkow, K. A. *Ber.* **60** (1927) 1104.
2. Halmøy, E., and Hassel, O. *Z. physik. Chem.* **B 15** (1932) 472.
3. Harries, C. *Ber.* **45** (1912) 814.
4. Zelinsky, N., and Gorsky, A. *Ber.* **41** (1908) 2483.
5. Wang Lund, E. *Acta Chem. Scand.* **4** (1950) 1109.
6. Hassel, O., and Wang Lund, E. *Acta Cryst.* **2** (1949) 309.
7. Bastiansen, O., Ellefsen, Ø., and Hassel, O. *Research* **2** (1949) 248.
8. Ellefsen, Ø., Hassel, O., and Wang Lund, E. *Acta Chem. Scand.* **4** (1950) 1145.
9. Willgerodt, C. *J. prakt. Chem.* [2] **35** (1887) 416.
10. Oiwa, T., Yamada, R., Hamada, M., Inouye, M., and Ohno, M. *Botyu-Kagaku* **15** (1950) 32.
11. Crossley, A. W. *J. Chem. Soc. Lond.* **85** (1904) 1416.

Received November 9, 1950.