

Tetrachloro-Cyclohexanone and Tetrachloro-Cyclohexanol Obtained from Cyclohexanol

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When cyclohexanol is chlorinated in sunlight or strong artificial light considerable quantities of a colourless solid substance of m.p. 84° C are deposited which, according to analysis, has the composition $C_6H_6Cl_4O$. Some crystals of the same substance have been obtained also when cyclohexanone was chlorinated under corresponding conditions. In the latter case, however, the chlorination usually leads to a breaking of the carbon ring and the formation of hexenal and (when water is present) caproic acid and adipic acid.

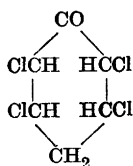
The chemical properties of this new compound (I) are rather interesting. Although the results of our investigation leave no doubt as to the correctness of the assumption that it is, in fact, a tetrachloro-cyclohexanone, the chemical reactivity of the keto group is strongly sterically hindered and it does not react with the ordinary keto-group reagents like hydroxylamine, phenylhydrazine or semicarbazide. In this respect it resembles chloranil, and surpasses the lower substituted quinones.

The reduction of the carbonyl group is possible, however, when aluminium isopropylate is used. This reaction takes place rather slowly, but the acetone formed in the course of it clearly proves the presence of a keto group in the molecule. When the reaction is finished, a colourless crystalline substance (II) melting at 62° C and having a composition corresponding to the formula $C_6H_8Cl_4O$, may be isolated from the reaction mixture.

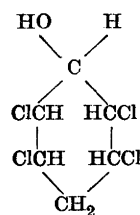
The alcoholic character of this new substance (II) is not easily demonstrated, as no derivatives could be obtained by the action of phenylisocyanate, diazomethane, or acid chlorides. A series of experiments were also carried out with the aim of replacing the hydroxy group by chlorine, but without any success. A strong steric hindrance must therefore be present in the reduction product as well.

A further interesting property of the ketone (I) is its behavior towards alkalis. Cold, dilute solutions of barium hydroxide easily brings the substance into solution, four equivalents of alkali thereby being neutralized. From this solution the entire content of chlorine is immediately precipitated with silver nitrate after the solution has been acidified with nitric acid. If, on the other hand, the solution of the ketone in barium hydroxide is heated with an excess of the alkali more barium hydroxide is neutralized and a crystalline precipitate is formed. We have not, so far, examined the precipitate thus obtained. The products obtained by cold hydrolysis using dilute alkaline solutions (ammonia, potassium hydroxide or barium hydroxide) appear to be rather complex, and we have not tried to isolate any of its components.

If the substance I is heated to 260—270° C hydrogen chloride is evolved and 2,6-dichlorophenol is formed. This seems to indicate that two of the chlorine atoms of the tetrachloro-cyclohexanone are linked to carbon atoms adjacent to the carbonyl group. We have started an electron diffraction investigation of the vapour of this substance, using the rotating sector method and from this we hope to be able to get more precise information concerning the positions of the chlorine atoms in the molecule. So far the results obtained seem to confirm that the structural formula I, based on the chemical properties of the substance, is the correct one.



I



II

It seems rather probable that our substance I corresponds to the tetrabromocyclohexanone of m.p. 119° C prepared by Boudroux and Taboury¹. The properties of this substance are indeed strikingly similar to those of substance I. It is easily hydrolysed by alkalis, splits off hydrogen bromide when heated, thus giving 2,6-dibromophenol², and fails to react with the ordinary keto-group reagents.

We have prepared the bromine compound, as described in Boudroux and Taboury's paper, and compared the crystals of this substance with those of our substance I. The results of the analysis, which E. Wang Lund was kind enough to carry out, are summarized in Table 1.

Table 1. Crystallographic characteristics of the two tetrahalogen-cyclohexanones.

$C_6H_6OCl_4$	$C_6H_6OBr_4$
Orthorhombic with 4 molecules in the unit cell	Orthorhombic with 4 molecules in the unit cell
$a = 8.79 \text{ \AA}$	$a = 10.9 \text{ \AA}$
$b = 16.4 \text{ \AA}$	$b = 14.7 \text{ \AA}$
$c = 6.23 \text{ \AA}$	$c = 6.28 \text{ \AA}$

Although the unit cells are very similar and the ratio of the molecule volumes approximately such as would be anticipated for analogous bodies, we still hesitate in expressing the view that they are strictly isomorphous because one of the lattice constants is actually *smaller* in the bromine compound than in the chlorine compound. The development of the crystals is also different, the chlorine compound usually forming needles, the bromine compound plates.

EXPERIMENTAL PART

Tetrachloro-cyclohexanone (I)

Bubbles of gaseous chlorine were led through a water-cooled glass flask containing cyclohexanol directly exposed to sunlight or artificially illuminated. Hydrogen chloride was evolved, and soon considerable quantities of colourless crystals were formed. After separation from the mother liquid and washing with carbon tetrachloride, the substance was recrystallized from carbon tetrachloride or ligroin. The needle-shaped crystals thus obtained were well developed and melted at 84°C .

$C_6H_6Cl_4O$	Calc.	C 30.54	H 2.56	Cl 60.11	Mol. wt. 236
	Obs.	» 29.68	» 2.61	» 59.50	» » 235 (benzene solution)

Tetrachloro-cyclohexanol (II)

10 g of I were treated with aluminium isopropylate, according to Lund³. Traces of acetone are present in the distillate from the beginning of the experiment, but the reaction is very slow. After 50–60 hours no further formation of acetone could be detected. The isopropyl alcohol was evaporated, *in vacuo*, and the remaining solid was treated with dilute sulphuric acid. The tetrachloro-cyclohexanol formed during the reaction was steam distilled and extracted from the distillate with ethyl ether. The ether solution was dried with anhydrous sodium sulphate and evaporated, and the remaining nearly colourless oil left to crystallize. After two recrystallizations from methanol, about 7 g of the new substance were obtained forming thick needles of m. p. 62°C . The alcohol is more sensitive to high temperatures than the corresponding ketone, and even at room

temperature it cannot be kept for any length of time without marked decomposition. It is more resistant towards alkalis, however, than the ketone.

$C_6H_8Cl_4O$	Calc.	C 30.28	H 3.39	Cl 59.60	Mol. wt. 238
	Obs.	» 30.46	» 3.40	» 60.21	» » 236 (benzene solution)

Hydrolysis of I

Cold, dilute sodium hydroxide solution was employed, and the remaining small excess of alkali titrated with 0.1 *N* hydrochloric acid. The hydrolysis of 0.1244 g of I required 20.85 ml of 0.1 *N* sodium hydroxide corresponding to 59.5 % chlorine.

The hydrolysis of 0.1522 g of I with 0.1 *N* potassium hydroxide yielded 0.3661 g of silver chloride:

Calc. for four atoms of chlorine	Cl 60.11
Obs.	» 59.50

The hydrolysis products were also extracted with ethyl ether, the ether solution dried with anhydrous sodium sulphate, and the solvent evaporated. A colourless viscous liquid was obtained which contains unsaturated substances since it adds on bromine. On standing or when heated, the liquid takes on a dark colour.

If the hydrolysis is performed with an excess of aqueous barium hydroxide in the absence of carbon dioxide, and the solution is heated to the boiling point, more of the base is neutralized and a white precipitate is formed.

2,6-Dichlorophenol from I

Tetrachloro-cyclohexanone was heated in a spherical flask fitted with a vertical reflux condenser. The temperature of the condenser was kept at 85—90° C. When heated on the sand bath, at 260—270° C, a vigorous evolution of hydrogen chloride took place. When this had subsided, the substance remaining in the flask was allowed to distill: at 217° C almost the entire contents of the flask distilled over. The distillate had the sharp odour of the chloro-phenols and gave a violet colour with ferric chloride. The crystalline mass was recrystallized from petroleum ether giving colourless needles of 2,5-dichlorophenol of m. p. 67° C.

Monochloro-cyclohexanol

After removing substance I, some ethanol was added to the liquid chlorination product of cyclohexanol and the mixture kept at a temperature a little above 0° C for some time. New crystals were then deposited which after recrystallization from ethanol-water had a melting point of 121—122° C. This substance shows a marked association tendency in benzene solution: the cryoscopical molecular weight increasing markedly with the concentration.

g substance per 20 g benzene	0.5066	0.2418	0.1173
Mol. wt. observed	157	148	146
$C_6H_{10}OHCl$	Cl 26.34	H (hydroxy-) 0.75	Mol. wt. 135
Obs.	» 25.93	» » 0.69	

SUMMARY

By chlorination of cyclohexanol a tetrachlorocyclohexanone and a monochlorocyclohexanol were formed. The reduction of the former with aluminium isopropylate led to a tetrachlorocyclohexanol. Both the ketone and the tetrachloroalcohol exhibit strong steric hindrance to reactions with their functional groups. When treated with cold, dilute alkalis all chlorine atoms in tetrachlorocyclohexanone were split off, and on heating the hydrolysed products, additional barium hydroxide was neutralized. Some physical examinations of the tetrachlorocyclohexanone have been carried out.

REFERENCES

1. Boudroux, F., and Taboury, F. *Compt. rend.* **154** (1912) 1509.
2. Wallach, O. *Ann.* **343** (1905) 41.
3. Lund, H. *Ber.* **70** (1937) 1520.

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