

CHLORINATION OF 2,4,6-TRICHLOROPHENOL IN ACIDIC AQUEOUS MEDIUM

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The course of chlorination of 2,4,6-trichlorophenol (*I*) in water and approximately 20% sulfuric and hydrochloric acids has been investigated. In all these media the reaction gives primarily 2,4,6,6-tetrachloro-2,4-cyclohexadienone (*II*) which is subsequently chlorinated under formation of polychlorinated alicyclic ketones or isomerized to give the more stable 2,4,4,6-tetrachloro-2,5-cyclohexadienone (*III*), the precursor of further arising chlorinated 1,4-benzoquinones. The ratio of the arising polychlorinated alicyclic ketones to chlorinated 1,4-benzoquinones is significantly influenced by concentration of hydrogen chloride in the reaction medium. On the basis of model experiments, the reaction mechanism of exhaustive chlorination of 2,4,6-trichlorophenol has been suggested.

Chlorination of phenol or its mono- and dichloro derivatives is known¹⁻⁷ to afford primarily 2,4,6-trichlorophenol (*I*). This upon further chlorination gives various products depending on reaction conditions. The course of chlorination of phenol in sewage water is significantly influenced by the pH value of the medium². In an alkaline medium the aromatic nucleus is destructed⁸ and at the phenol-chlorine ratio 1 : 10 (w/w) aromatic compounds cannot be detected at all⁹. Eliášek and Jungwirth chlorinated 0.001% (ref.⁵) to 0.1% (ref.⁶) aqueous solutions of phenol at pH 2-3 and phenol-chlorine ratio 1 : 6 (w/w). After 24 h they obtained a mixture of the following chlorinated 1,4-benzoquinones in 60% yield: 2,6-dichloro-1,4-benzoquinone (*IV*), 2,3,5-trichloro-1,4-benzoquinone (*V*) and tetrachloro-1,4-benzoquinone (*VI*) (ref.⁶). Müller and Linde⁷, who chlorinated concentrated acidic aqueous phenol dispersions, studied the time dependence of the content of chlorine and carbonyl groups in the product and concluded that the chlorination proceeds *via* 2,4,6-trichlorophenol (*I*) and only after this stage a more significant amount of chlorinated 1,4-benzoquinones is formed^{7,10}.

However, the results of the mentioned studies do not explain sufficiently the processes taking place in the chlorination of phenol or compound *I* in acidic aqueous media. Thus, *e.g.*, the formation of polychlorinated alicyclic ketones has been overlooked as the result of rather difficult analytical evaluation. The aim of the present work is to elucidate the course of the exhaustive chlorination of *I* in acidic aqueous media using analytical methods developed earlier by the author and coworkers¹⁴⁻¹⁸.

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EXPERIMENTAL

Synthesis of Model Compounds

The model compounds were prepared in chromatographic purity by described procedures: 2,4,6-trichlorophenol (*I*) was obtained by chlorination of phenol¹¹, 2,4,6,6-tetrachloro-2,4-cyclohexadienone (*II*), b.p. 43·0°C/16 Pa, by chlorination of *I* or its sodium salt (ref.¹¹), 2,4,4,6-tetrachloro-2,5-cyclohexadienone (*III*), m.p. 123·2°C, by chlorination of *I* (ref.¹²) or isomerization of *II* (ref.¹¹), 2,6-dichloro-1,4-benzoquinone (*IV*), m.p. 121–122·0°C, 2,3,5-trichloro-1,4-benzoquinone (*V*), m.p. 169·2–169·8°C, and tetrachloro-1,4-benzoquinone (*VI*), m.p. 294–295·0°C, by oxidation of the corresponding chlorinated phenols¹, 2,3,4,6,6-pentachloro-2,4-cyclohexadienone (*VII*), m.p. 29–29·4°C, by chlorination of 2,3,4,6-tetrachlorophenol or its sodium salt¹¹, 2,3,4,4,6-pentachloro-2,5-cyclohexadienone (*VIII*), m.p. 112–113·0°C, by isomerization of *VII* (ref.¹¹), and 2,2,3,4,5,6,6-heptachloro-3-cyclohexenone (*IX*), m.p. 95·7–96·6°C, by chlorination of *I* (ref.¹³). All the melting points are corrected.

Analysis of Reaction Products

The homogenized samples¹ were first qualitatively analyzed by thin-layer chromatography^{11,14,15}. Quantitative analysis was performed by gas-liquid chromatography^{16,17} (also in combination with mass spectrometry¹⁸), and IR spectroscopy¹.

Gas-liquid chromatographic analysis of reaction mixtures containing simultaneously the ketones *II*, *III*, *VII*, *VIII*, and *IX* and the chlorinated 1,4-benzoquinones *IV*–*VI* was complicated by decomposition of the ketones at temperatures above 125°C under formation of less chlorinated phenols¹⁸; enabling thus a determination of the sum of the isomeric ketones (*e.g.* *II* and *III*) at best. The use of lower temperature or a temperature program was not suitable for analyses of *IV*–*VI* which were not eluted under the given conditions or their peaks coincided with those of the ketones. Both groups of compounds were therefore separated on the basis of their different solubility in warm *n*-heptane or tetrachloromethane¹. Fractional crystallization afforded three fractions of which the first contained *VI*, the second *IV* and *V*, and the third a mixture of the ketones *II*, *III*, *VII*–*IX*, and in some cases also *I*. The content of *IV*–*VI* in the first two fractions was determined by gas-liquid chromatography¹⁶. The amount of the ketones in the third fraction was estimated by quantitative IR spectroscopy; however, at lower concentrations of one of the isomeric ketones it was possible to determine only their total amount¹. In the gas-liquid chromatographic analysis of the reaction mixtures containing, in addition to compounds *II*–*IX*, compound *I* or 2,3,4,6-tetrachlorophenol, it was necessary to convert the chlorophenol to a more volatile derivative and to determine the corresponding ketone as free chlorophenol¹⁸. More volatile chlorophenol derivatives were prepared by treatment with diazomethane, analogously to ref.¹⁷. In this reaction the ketones *II*, *III*, *VII*–*IX* remain intact, whereas the chlorinated 1,4-benzoquinones *IV*–*VI* give compounds¹⁹ that are not eluted under the given conditions¹.

Chlorination

The chlorinations were performed at 75°C under constant hydrodynamic conditions in a previously described apparatus¹; the weight ratio of the chloro derivative (*I*, *II* or *VII*) to the reaction medium was about 1 : 10 to 1 : 11. All the obtained values are means of two independent experiments.

Chlorination of compound I. Compound *I* (19.75 g; 0.01 mol) was suspended in water (200 ml) or in 20.13% sulfuric acid (200 ml) or in 20.84% hydrochloric acid (200 ml). Chlorine was introduced into the reactor at $75 \pm 0.5^\circ\text{C}$. After the end of chlorination, the content of the reactor was extracted with several portions of benzene (total amount about 800 ml) until no organic compounds were detected by the thin-layer chromatography of the last extract. The combined benzene extracts were dried over anhydrous sodium sulfate and the solvent was evaporated under diminished pressure (bath temperature below 45°C). Since the obtained residue was not homogeneous, it was dissolved in a suitable solvent prior to further analyses. The solubility of the product was influenced by the amount of *VI*. Acetone or benzene or their mixtures proved to be the best solvents. After the extraction, the content of hydrochloric acid in the aqueous phase was determined by titration with silver nitrate according to Mohr²⁰ and then the water was evaporated *in vacuo* at temperatures lower than 50°C . The sulfuric acid-containing aqueous phases were neutralized with sodium carbonate solution and the obtained solution was evaporated to dryness. The residue was extracted with acetone for 6 h and the extract was taken down at a reduced pressure (bath temperature below 40°C). The pertinent experimental data are given in Tables I–III.

Chlorination of compound II. The ketone *II* (4.70 g; 0.02 mol) was added at $75 \pm 0.1^\circ\text{C}$ to a solution of chlorine (0.1 g) in 20.78% hydrochloric acid (50 ml). Chlorine (total 1.40 g; 0.02 mol) was introduced into the formed suspension. The content of the reactor was extracted with benzene, the extract dried over anhydrous sodium sulfate and benzene evaporated under diminished pressure (bath temperature below 35°C), yielding 5.45 g of a residue whose composition is given

TABLE I
Products of chlorination of compound *I* in water

Amount of chlorine mol/mol <i>I</i>	0.51	1.00	1.50	2.02	2.50	3.00
Chlorination time, min	75	135	200	320	490	1 260
Formed HCl, mol/mol <i>I</i>	1.33	2.50	3.65	4.27	4.77	5.21
Isolated organic material, g	18.95	17.74	18.25	18.60	19.15	20.30
Product isolated from aqueous acidic phase, g ^a	0.30	0.60	0.95	1.10	1.45	1.55
Composition of the organic material mol/mol <i>I</i>						
<i>I</i>	0.58	0.37	0.21	0.07	0.02	0.002
<i>II</i> + <i>III</i>	0.15	0.20	0.24	0.09	0.05	0.01
<i>IV</i>	0.16	0.29	0.39	0.47	0.11	0.003
<i>V</i>	0.01	0.01	0.04	0.12	0.38	0.40
<i>VI</i>	—	<0.001	0.01	0.01	0.12	0.15
<i>VII</i> + <i>VIII</i>	0.04	0.06	0.06	0.07	0.07	0.04
<i>IX</i>	—	—	—	—	0.01	0.04

^a Composition is analogous to that of oily compounds arising in hydrolysis of ketone *III* (ref.²¹).

in Table IV. Thus, exhaustive chlorination of *II* with 2.10 g (0.03 mol) of chlorine afforded 5.43 g of the residue (Table IV). In an analogous way, ketone *II* was chlorinated in water and 20.13% sulfuric acid, affording 4.58 g and 5.04 g, respectively, of red-yellow semicrystalline material of composition given in Table IV; however, these chlorinations were not well reproducible.

Chlorination of compound VII. Ketone *VII* (4.00 g; 0.015 mol) was added at $75 \pm 0.1^\circ\text{C}$ to a solution of chlorine (0.20 g) in 20.78% hydrochloric acid (40 ml) and the formed suspension was chlorinated with 1.05 g (0.015 mol) of chlorine. The reaction mixture was extracted with benzene, the extract dried over anhydrous sodium sulfate and the solvent evaporated *in vacuo* at a temperature lower than 40°C . The residue contained 18.6% (w) of the ketone *IX* and 80.2% (w) of the ketone *VIII*.

Isomerization

Isomerization of compound II. A suspension of ketone *II* (4.64 g; 0.02 mol) in 20.78% hydrochloric acid (50 ml) was stirred at $75 \pm 0.1^\circ\text{C}$ for 30–120 min. After cooling, the reaction mixture was extracted with benzene. The benzene extract was dried over anhydrous sodium sulfate and evaporated *in vacuo* at a temperature lower than 40°C , affording 4.39 g of a yellow crystalline material of composition given in Table V. Similarly was isomerized the ketone *II* in water or 20.13% sulfuric acid; yield 3.38 g and 3.80 g, respectively, of a red oil in which only compounds listed in Table V were identified.

Isomerization of compound VII. A suspension of ketone *VII* (4.00 g; 0.015 mol) in 20.78% hydrochloric acid (40 ml) was stirred at $75 \pm 0.1^\circ\text{C}$ for 4 h. After cooling, the crystalline product

TABLE II

Products of chlorination of compound *I* in 20.13% sulfuric acid

Amount of chlorine mol/mol <i>I</i>	0.50	1.02	1.35	1.51	2.00	2.46
Chlorination time, min	35	80	130	165	220	1 260
Formed HCl, mol/mol <i>I</i>	1.35	2.20	2.84	3.03	3.96	4.64
Isolated organic material, g	18.70	19.10	19.45	19.55	19.85	20.90
Product isolated from aqueous acidic phase, g ^a	0.03	0.03	0.03	0.03	0.05	0.05
Composition of the organic material mol/mol <i>I</i>						
<i>I</i>	0.60	0.33	0.19	0.15	0.05	0.006
<i>II</i> + <i>III</i>	0.11	0.25	0.30	0.25	0.04	0.02
<i>IV</i>	0.19	0.28	0.31	0.28	0.05	<0.001
<i>V</i>	0.01	0.03	0.05	0.15	0.48	0.30
<i>VI</i>	—	—	—	<0.001	0.04	0.30
<i>VII</i> + <i>VIII</i>	0.02	0.04	0.06	0.07	0.13	0.10
<i>IX</i>	—	—	—	—	0.02	0.04

^a Unidentified products.

was taken up in benzene, the organic extract dried over sodium sulfate and taken down at a temperature lower than 40°C. Yield 3.85 g of a crystalline product containing 97.5% (w) of the ketone *VIII*, 2% (w) of 2,3,4,6-tetrachlorophenol, and 0.5% (w) of the unreacted ketone *VII*.

RESULTS AND DISCUSSION

In accord with Scheme 1, chlorination of compound *I* in water and 20.12% sulfuric acid (2.5 mol of chlorine to 1 mol of *I*) affords mainly the chlorinated 1,4-benzoquinones *IV*–*VI* (about 0.6 mol/mol of *I*) and only minor amounts of the polychlorinated alicyclic ketones *III*, *VII*–*IX* (up to 0.15 mol/mol of *I*) (Table I and II). The remaining part of the product consists of unidentified oily compounds the character of which was already discussed²¹. Following chlorination of the compound *I* proceeds only slowly, the maximum consumption of chlorine being about 3 mols per 1 mol of *I*; at this stage the portion of unidentified products both in the organic and acidic aqueous phases increases²¹ (Table I).

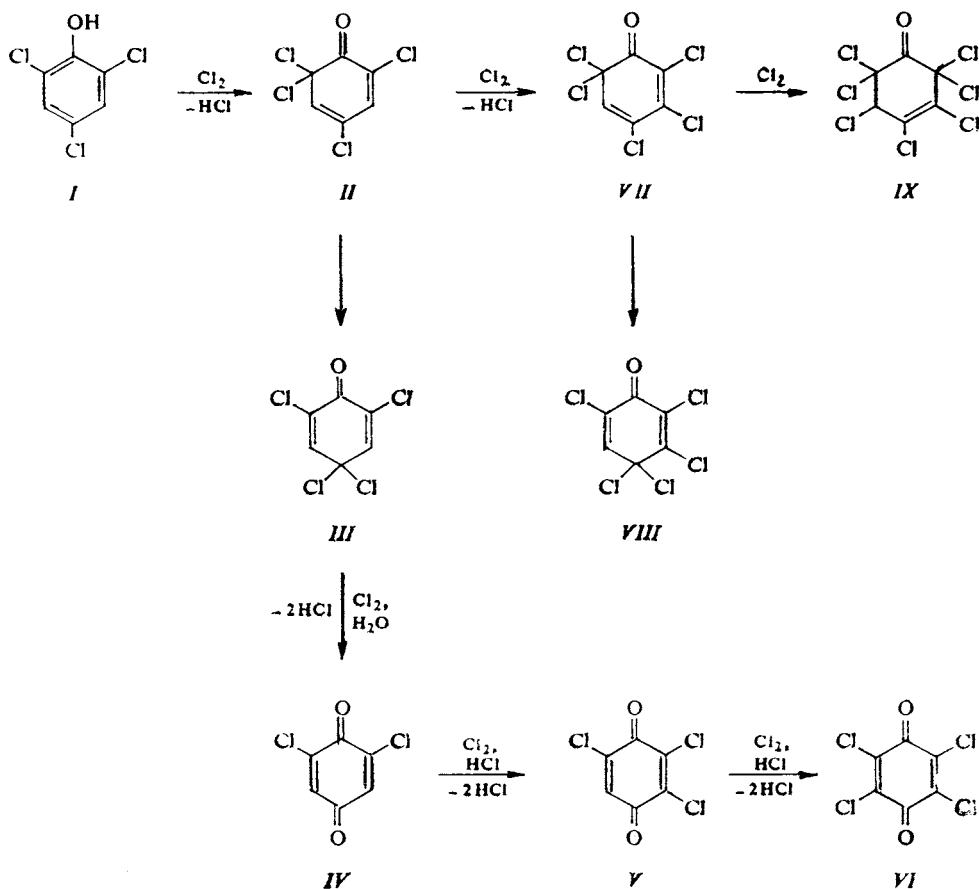
The principal products of exhaustive chlorination of compound *I* in 20.84% hydrochloric acid (2.5 mol Cl₂/mol of *I*) are the polychlorinated alicyclic ketones *VIII*

TABLE III
Products of chlorination of compound *I* in 20.84% hydrochloric acid

Amount of chlorine mol/mol <i>I</i>	0.25	0.53	1.01	1.53	2.00	2.55
Chlorination time, min	40	63	114	190	320	1 290
Formed HCl, mol/mol <i>I</i> ^a	0.30	0.70	1.25	1.59	2.05	2.58
Isolated organic material, g	19.75	20.55	21.40	23.10	24.60	27.50
Product isolated from aqueous acidic phase, g ^b	0.03	0.05	0.06	0.05	0.02	0.15
Composition of the organic material mol/mol <i>I</i>						
<i>I</i>	0.84	0.70	0.47	0.26	0.11	0.006
<i>II</i> + <i>III</i>	0.07	0.16	0.10	0.05	0.03	<0.001
<i>IV</i>	0.03	0.02	0.02	0.02	0.01	<0.001
<i>V</i>	0.01	0.02	0.05	0.06	0.08	0.01
<i>VI</i>	—	0.01	0.08	0.10	0.19	0.25
<i>VII</i>	0.04	0.06	0.20	0.07	0.01	<0.001
<i>VIII</i>	—	<0.001	0.04	0.34	0.44	0.53
<i>IX</i>	—	<0.001	0.003	0.01	0.05	0.14

^a The values are somewhat distorted due to loss of hydrogen chloride from the chlorination apparatus; ^b unidentified products; chlorinated hydroquinones were not found.

and *IX* (about 0.7 mol/mol of *I*), the rest being mainly tetrachloro-1,4-benzoquinone (*VI*) (up to 0.25 mol/mol of *I*) (Table III).



SCHEME 1

From the chlorination data given in Tables I–III it is evident that the quantitative differences in the product composition in the given media depend on sufficiently high concentration of hydrochloric acid. This is, however, not a mere effect of proton concentration, since 20% sulfuric acid also contains a high concentration of protons, yet the results of exhaustive chlorination of compound *I* are similar to those obtained in water. Therefore, the different results must be due to the behaviour of one of the intermediates arising during the chlorination.

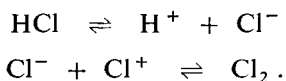
As we have found already previously, such key compound whose fate is most influenced by hydrogen chloride concentration in the reaction mixture is 2,4,6,6-tetrachloro-2,4-cyclohexadienone (*II*). The inductive effect of the symmetrically placed chlorine atoms in the enol form of compound *I* facilitates further chlorination of *I* to give the keto form of compound *II*. Its formation depends on the ease of formation of the trichlorophenoxide anion by loss of proton and subsequent isomerization and chlorination²¹. The requirements for this reaction are met in principle in all but extremely acidic reaction media in which the cleavage of proton from the compound *I* is impossible. This holds first of all for strong acids which are known to stabilize the enol forms²².

The formation of ketone *II* in the chlorination of *I* was proved by thin-layer chromatography^{11,14} as well as by the gas-liquid chromatography – mass spectrometry method¹⁸. Because of fast isomerization and chlorination of *II* and its complicated determination it was not possible to determine quantitatively the ketone *II* in the presence of its more stable isomer, 2,4,4,6-tetrachloro-2,5-cyclohexadienone (*III*) in the complex reaction mixtures. Therefore only sums of *II* and *III* are given in Tables I–III. According to the thin-layer chromatography, the concentration of *II* was invariably 1.5 to 2 orders of magnitude lower than that of *III*.

The course of chlorination of *I* according to Scheme 1, particularly the formation of the polychlorinated alicyclic ketones *III*, *VII–IX*, was confirmed by model experiments with chromatographically pure ketone *II* (Tables IV and V).

Isomerization of ketone *II* in water and dilute sulfuric acid afforded red oily compounds which were difficult to identify. In addition to the more stable isomer *III*, the reaction mixture contained up to 0.1 mol of compound *I* (based on one mol of starting *II*) and traces of the chlorinated 1,4-benzoquinones *IV–VI*. As seen, the character of the reaction products is the same as the character of compounds arising in the hydrolysis of ketone *III* in water and sulfuric acid²¹.

The results of isomerization of *II* in hydrochloric acid are, however, qualitatively different (Table V). In the absence of chlorine, ketone *II* is obviously isomerized to give ketone *III*. Only a small amount of *III* gives the chlorinated 1,4-benzoquinones *IV–VI*, the greatest part remaining unreacted. Simultaneously, a significant amount of 2,3,4,4,6-pentachloro-2,5-cyclohexadienone (*VIII*) was observed. Since, in the given medium, direct chlorination of *III* to *VIII* is out of question¹, we assume that the chlorine cation, arising by cleavage from the ketone *II* (ref.²¹), can produce elemental chlorine from hydrochloric acid according to the equations:



The formed elemental chlorine can then chlorinate the unreacted ketone *II* to give 2,3,4,6,6-pentachloro-2,4-cyclohexadienone (*VII*) which under the given conditions

isomerizes almost completely to the more stable derivative *VIII*. Since the concentration of the arising elemental chlorine is proportional to that of the reacted ketone *II*

TABLE IV
Products (mol/mol) *II* of chlorination of ketone *II*

Reaction medium	Water	20.13% H ₂ SO ₄	20.78% HCl	
Reaction time, min	180	205	230	300
Amount of chlorine, mol/mol <i>II</i>	1.07	1.07	1.07	1.57
<i>I</i>	0.03	0.02	0.02	0.01
<i>II</i>	^a	^a	^a	—
<i>III</i>	0.32	0.28	0.05	0.01
<i>IV</i>	0.27	0.02	<0.001	0.01
<i>V</i>	0.04	0.30	0.02	0.03
<i>VI</i>	0.02	0.04	0.18	0.18
<i>VII</i>	0.05	0.05	0.16	0.09
<i>VIII</i>	0.07	0.17	0.51	0.51
<i>IX</i>	—	—	<0.001	0.09

Traces of the compound identified by thin-layer chromatography.

TABLE V
Products (mol/mol *II*) of isomerization of ketone *II*

Reaction medium	Water	20.13% H ₂ SO ₄	20.78% HCl	
Reaction time, min	60	60	60 ^a	120
<i>I</i>	0.08	0.10	0.29	0.29
<i>II</i>	^b	^b	^b	^b
<i>III</i>	0.05	0.05	0.35	0.34
<i>IV</i>	^b	^b	<0.001	^b
<i>V</i>	^b	<0.001	0.01	<0.001
<i>VI</i>	<0.001	<0.001	0.04	0.05
<i>VII</i>	—	—	<0.001	<0.001
<i>VIII</i>	—	—	0.23	0.23

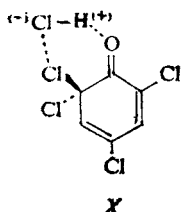
^a Identical results obtained also after 30 min; ^b traces of the compound identified by thin-layer chromatography.

(its oxo-enol isomerization gives the trichlorophenolate anion which reacts with proton to give *I*), it is obvious that the excess of the chlorination agent is consumed in the oxidation of chlorinated hydroquinones (whose formation in the medium with a high concentration of hydrogen chloride must be assumed) producing the corresponding chlorinated 1,4-benzoquinones *IV–VI* (ref.²¹).

Chlorination of the ketone *II* afforded qualitatively the same results as chlorination of the phenol *I* (Table V). In water and dilute sulfuric acid the isomerization of *II* to the more stable *III* is preferred, the latter giving then the chlorinated 1,4-benzoquinones *IV–VI* (ref.²¹). Concurrent chlorination of ketone *II* gives only small amounts of ketones *VII* and *VIII* (about 0.2 mol per mol of the starting *II*). At the same time, other chlorination reactions of ketones *II* and *III* (as evidenced by the proven presence of *I*) take place leading to minor quantities of red, unidentified oils²¹.

Chlorination of the ketone *II* in hydrochloric acid affords a mixture of ketones *VII–IX* (about 0.7 mol per mol of the starting *II*) in addition to the chlorinated 1,4-benzoquinones *IV–VI* (about 0.2 mol per mol of the starting *II*). This confirms the assumption that in this medium the chlorination of compound *II* prevails over its isomerization. The ketone *VII*, formed by substitution chlorination of *II*, is the precursor of further two compounds: ketone *VIII* and 2,2,3,4,5,6,6-heptachloro-3-cyclohexenone (*IX*). Model experiments proved that these compounds arise from ketone *VII* by isomerization and addition of chlorine, respectively (Scheme 1). Under the given reaction conditions, the isomerization into the more stable isomer *VIII* is preferred (about 0.8 mol per mol of the starting *VII*) since the chlorination of *VII* to *IX* is obviously difficult. Both these reactions are less sensitive towards hydrogen chloride concentration than in the case of the ketone *II*.

As follows from the above discussion, in the chlorination of *I* or *II* the ratio of the formed polychlorinated alicyclic ketones to the chlorinated 1,4-benzoquinones is influenced by hydrogen chloride concentration in the reaction medium. The balance of hydrogen chloride arising in the exhaustive chlorination of *I* in the given reaction systems is very complex. Hydrogen chloride arises by reactions leading to compounds *II*, *IV*, and *VII* and adds simultaneously to the arising 1,4-benzoquinones *IV* and *V* (Scheme 1; ref.²¹). The found balance of hydrogen chloride in the reaction systems agrees with that calculated according Scheme 1.



In order to explain the different effect of hydrochloric acids we suggest the formation of a complex (X) between the ketone *II* and HCl. This inhibits the isomerization of the ketone *II* into the ketone *III* in the medium of high initial concentration of hydrogen chloride and at the same time promotes its further chlorination in the *meta*-position to give the ketone *VII*.

Ketone *III*, formed by isomerization of *II*, is the precursor of the chlorinated 1,4-benzoquinones *IV*–*VI*. Compound *IV* arises *via* a chlorine cation or proton²¹, a condition which is fulfilled in the given media. The compounds *V* and *VI* are not formed by substitution chlorination of *IV* but by addition of hydrogen chloride to the starting chlorinated 1,4-benzoquinones *IV* and *V* followed by a very fast oxidation of the arising chlorinated hydroquinones by chlorine²¹.

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