

Study of the reaction products of 2,2,5,5-tetrakis(halogenomethyl)-cyclopentanone with potassium cyanide

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The reaction of 2,2,5,5-tetrakis(chloromethyl)- and -(bromomethyl)cyclopentanone with potassium cyanide in 98% ethanol resulted in the formation of 1,3-epoxides. Their structures were proved by i.r., u.v., ¹H-n.m.r., and mass spectra. With hydrohalic acids they afforded oxonium salts which were thermally split into tetrakis(halogenomethyl)cyclopentanones.

После реакции 2,2,5,5-тетраakis(хлорметил)- и -(бромметил)-циклопентанонов с цианистым калием в 98%-ном спирте были изолированы 1,3-эпоксиды. Их структура была подтверждена на основании интерпретации инфракрасных, ультрафиолетовых, ¹H-ЯМР и масс-спектров. Они реагируют с галогеноводородными кислотами с образованием оксониевых солей, которые термически расщепляются на тетраakis(галогенметил)циклопентаноны.

In the scope of the study of utilization of different 2,2,5,5-tetrakis(hydroxymethyl)cyclopentanone (THCP) derivatives in macromolecular chemistry, we studied the halogen derivatives prepared according to [1]. Originally we aimed at substitution of four halogens by nitrile groups and, by subsequent hydrolysis, at obtaining tetracarboxylic acid suitable for polymerization reactions. However, this reaction resulted in the formation of 1,3-epoxides and the reaction mechanism was in agreement with the work of *Gerner et al.* [2]. These authors studied the solvolysis of tosyl esters of THCP and isolated 1,3-epoxides as well. Our results were proved also by the papers [3—12] dealing with aliphatic halogenoketones and reporting that aliphatic halogenoketones with alkali cyanides afforded in most cases epoxides, probably by cyclization of cyanohydrins, and not the appropriate nitriles.

Table 1
Review of the prepared compounds

No.	Formula	M	Calculated/found					Yield %	M.p., °C Solvent	Value R_f
			% C	% H	% N	% X	% Y			
I	C ₁₀ H ₁₂ Cl ₃ NO	268.56	44.72	4.50	5.21	39.60 (Cl)	—	80	89 Ethanol	0.68
			44.85	4.46	5.36	39.34 (Cl)	—			
II	C ₁₀ H ₁₃ Cl ₄ NO	305.02	39.36	4.26	4.59	46.50 (Cl)	—	75	189—191 ^b Chloroform	0.59
			39.56	4.19	4.61	46.60 (Cl)	—			
III	C ₁₀ H ₁₃ BrCl ₃ NO	349.47	34.36	3.75	4.00	30.43 (Cl)	22.86 (Br)	85	178—180 ^b Chloroform	0.60
			34.56	3.86	4.07	30.42 (Cl)	22.90 (Br)			
IV	C ₉ H ₁₂ Cl ₄ O	277.99	38.88	4.35	—	51.01 (Cl)	—	95 ^c 80 ^d	71.5 ^a Ethanol	0.78
			38.70	4.35	—	51.10 (Cl)	—			
V	C ₉ H ₁₂ BrCl ₃ O	319.47	33.57	3.75	—	33.00 (Cl)	24.82 (Br)	95 ^c 82 ^d	65—67 Carbon tetrachloride	0.79
			33.59	3.96	—	33.15 (Cl)	24.90 (Br)			
VI	C ₁₀ H ₁₂ Br ₃ NO	401.92	29.88	3.01	3.48	59.64 (Br)	—	70	121—122 Ethanol	0.83
			29.80	3.05	3.45	59.52 (Br)	—			
VII	C ₁₀ H ₁₃ Br ₃ ClNO	438.38	27.40	2.30	3.20	8.09 (Cl)	54.68 (Br)	70	188—190 ^b Chloroform	0.61
			27.30	2.10	3.10	7.90 (Cl)	54.50 (Br)			
VIII	C ₁₀ H ₁₃ Br ₄ NO	482.84	24.87	2.69	2.90	66.19 (Br)	—	80	200—202 ^b Chloroform	0.62
			24.60	2.50	2.70	66.02 (Br)	—			
IX	C ₉ H ₁₂ Br ₄ O	455.82	23.71	2.65	—	70.12 (Br)	—	94 ^c 82 ^d	91.5 ^e Ethanol	0.91
			23.90	2.60	—	70.30 (Br)	—			
X	C ₉ H ₁₂ Br ₃ ClO	411.36	26.27	2.90	—	8.61 (Cl)	58.27 (Br)	92 ^c 80 ^d	83—85 Ethanol	0.89
			26.05	2.60	—	8.52 (Cl)	58.10 (Br)			

a) Melting point according to [1] 71.5°C.

b) Melting point determined in capillary.

c) Yield obtained by the method A.

d) Yield obtained by the method B.

e) Melting point according to [1] 91.5°C and [18] 91°C.

Experimental

Melting points were measured on a Kofler block. The purity of the prepared compounds was controlled by thin-layer chromatography on Silufol 654 141 in the system benzene—methanol (8:2). The compounds were visualized by iodine vapours and the Dragendorff reagent. The results of elemental analyses, melting points, yields, and the R_f values are presented in Table 1.

The starting 2,2,5,5-tetrakis(hydroxymethyl)cyclopentanone and its halogen derivatives were prepared according to [1].

Ultraviolet spectra were measured on a Specord UV VIS (Zeiss, Jena) spectrophotometer in ethanol of spectral grade; concentration 10^{-2} and 10^{-3} M.

Infrared spectra were measured on a double-beam UR-10 (Zeiss, Jena) spectrophotometer in the region of $3500\text{--}670\text{ cm}^{-1}$ in KBr pellets, paraffin oil suspension as well as in 0.1 M chloroform solutions.

$^1\text{H-n.m.r.}$ spectra were measured on a Tesla DS 487 A apparatus in CDCl_3 at working frequency 80 MHz using tetramethylsilane as a standard.

The results of i.r., u.v., and $^1\text{H-n.m.r.}$ spectra are presented in Tables 2—4.

Table 2

Infrared spectra in paraffin oil suspension

No.	$\bar{\nu}(\text{C}=\text{O})$ cm^{-1}	$\bar{\nu}(\text{CN})$ cm^{-1}	$\bar{\nu}_{\text{as}}(\text{C}-\text{O}-\text{C})$ $\bar{\nu}_{\text{s}}(\text{C}-\text{O}-\text{C})$ cm^{-1}	$\bar{\nu}(\text{OH})$ cm^{-1}
I	—	2245	985 965	—
II	—	2251	—	3335
III	—	2250	—	3330
IV	1737	—	—	—
V	1744	—	—	—
VI	—	2240	972 962	—
VII	—	2250	—	3330
VIII	—	2250	—	3330
IX	1747	—	—	—
X	1749	—	—	—

Mass spectrum of the compound I was taken on an MS-9025 mass spectrometer at the emission of 10 mA, electron energy of 70 eV and 70°C . The spectrum of the compound V was measured on an MCh 1305 mass spectrometer at the emission of 1 mA, electron energy of 70 eV and 40°C .

Table 3

Ultraviolet spectra

No.	Band I		Band II		Band III		Band IV	
	λ_{\max} nm	ϵ	λ'_{\max} nm	ϵ	λ''_{\max} nm	ϵ	λ'''_{\max} nm	ϵ
IV	320 sh	20	316	41	307	46	297 sh	38
V	330 sh	50	316	80	309	90	298 sh	70
IX	333 sh	37	318	79	307	82	297 sh	68
X	330 sh	30	318	68	305	72	297 sh	53

sh — shoulder.

Table 4

¹H-n.m.r. spectra
 δ (p.p.m.)

No.	—CH ₂ — in cyclopentane ring	—CH ₂ X (X = Cl, Br)	—CH ₂ O—
I	1.87—2.43 (m,8H) ^a	3.25—4.06 (m,6H) ^a	4.40 (k,2H) ^c
IV	2.18 (s,4H) ^b	3.36—3.80 (m,8H) ^a	—
V	2.25 (s,4H) ^b	3.30—3.85 (m,8H) ^a	—
VI	2.30—2.95 (m,4H) ^a	3.60—4.40 (m,6H) ^a	4.85 (k,2H) ^c
IX	2.70 (s,4H) ^b	3.80—4.20 (m,8H) ^a	—
X	2.70 (s,4H) ^b	3.80—4.30 (m,8H) ^a	—

a) m — multiplet; H — hydrogens.

b) s — singlet; H — hydrogens.

c) k — quartet; H — hydrogens.

2,2,5-Tris(X-methyl)-1-cyano-7-oxabicyclo(3,2,0)heptane
(X = Cl I; Br VI)

Potassium cyanide (10 g; 0.16 mole) was heated in 98% ethanol (50 ml) under reflux. Then tetrakis(X-methyl)cyclopentanone (27.8 g; 0.1 mole) in ethanol (200 ml) was added. The mixture was heated on a water bath for 10 h, then ethanol was distilled off and the product was crystallized.

The mass spectrum of the compound I: m/e 188 = M — CH₂Cl — CH₂O, 218 = M — CH₂Cl, 232 = M — HCl.

2,2,5-Tris(X-methyl)-1-cyano-7-oxoniabicyclo(3,2,0)heptane halogenide
(hal = Cl, X = Cl II ; Br, Cl III ; Cl, Br VII ; Br, Br VIII)

The compounds *I* and *VI*, respectively, (10 g; 0.035 mole) were heated with concentrated hydrohalic acid (HCl, HBr) (250 ml) for 12 h under reflux. The product was filtered by suction, washed with water to neutral reaction, and crystallized.

2,2,5,5-Tetrakis(X-methyl)cyclopentanone
(X = Cl IV ; Br IX)

2,5,5-Tris(X-methyl)-2-Y-methylcyclopentanone
(X = Cl, Y = Br V ; Br, Cl X)

Method A

The compounds *II*, *III*, *VII*, and *VIII*, respectively, (0.05 mole) were allowed to sublime in a vacuum sublimator at the pressure of water pump and 190°C.

Method B

The compounds *II*, *III*, *VII*, and *VIII*, respectively, (0.05 mole) were heated in water (200 ml) for 10 h. The obtained product was filtered by suction and crystallized.

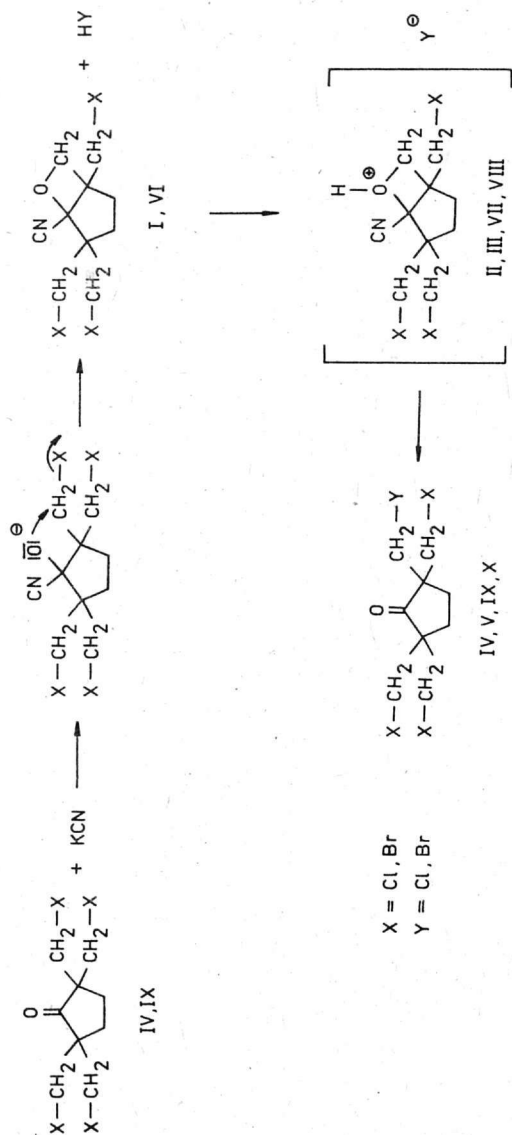
The mass spectrum of the compound *V*: m/e 91 = $O=C^{\oplus}-CH_2-CH_2-Cl$; m/e 105 = $M-Br-3HCl-CO$; m/e 141 = $M-Br-2HCl-CO$; m/e 177 = $M-Br-HCl-CO$; m/e 205 = $M-Br-HCl$; m/e 241 = $M-Br$; m/e 322 = M .

Results and discussion

The structure of the compounds resulting from the reactions of chloro and bromo derivatives of THCP with excess potassium cyanide in alcoholic solution was shown by elemental analysis and basic spectral data to be different from that of the awaited nitrile. Detailed study of the spectra of these derivatives showed that the carbonyl group reacted advantageously and the final products were 1,3-epoxides. Their structures were proved also by the reaction with hydrohalic acids (HCl, HBr) under the formation of oxonium salts which were thermally split into halogenoketones. The formation of these epoxides as well as their reactions with hydrohalic acids can be expressed by Scheme 1.

The obtained 1,3-epoxides were white well crystallizable substances stable when exposed to air and light. The appropriate iodo derivative with sodium cyanide did not lead to positive results; only the unchanged starting compounds were isolated.

Contrary to the starting halogen derivatives, the band $\nu(C=O)$ was not observed in the i.r. spectra of these compounds but bands belonging to $\nu(C-O-C)$



Scheme I

appeared in the region of $950\text{--}980\text{ cm}^{-1}$. The i.r. spectra measured in chloroform solutions did not show the presence of the bands belonging to stretching vibration of the C=N group. In KBr pellets and paraffin oil suspension, where the concentration of compounds was higher, a weak $\nu(\text{CN})$ vibration was observed at 2250 cm^{-1} . The decreased intensity of this band was proved also by other authors [13—15]. They reported that substitution on the carbon atom in α position by other groups, e.g. $-\text{CN}$, $-\text{OR}$, $-\text{NR}_2$, $-\text{NO}_2$, was in most cases accompanied only by a little change of frequency but by a great decrease of the band intensity. The intensity decreased in some cases so much that the vibration belonging to $-\text{CN}$ group was not observable. This change was probably in connection with the change of dipole moment of the nitrile molecule on substitution.

In the $^1\text{H-n.m.r.}$ spectra it was possible to identify signals of $-\text{CH}_2-$ groups in cyclopentanone ring and of $-\text{CH}_2\text{X}$ groups as multiplets. The signals of two protons in $-\text{OCH}_2-$ were observed as quartets.

The mass spectrum of the epoxide *I* showed a fragment ion m/e 188 which corresponded to the fragment $\text{M}-\text{CH}_2\text{Cl}-\text{CH}_2\text{O}$ and the ion 218 belonging to the fragment $\text{M}-\text{CH}_2\text{Cl}$. A molecular ion was not observed but the ion 232 belonging to the fragment $\text{M}-\text{HCl}$ was present. The bands belonging to the $n \rightarrow \pi^*$ transitions of the starting halogenoketones were not observed in the u.v. spectra.

The structures of the obtained 1,3-epoxides were further proved by reactions with hydrohalic acids (HCl, HBr). The appropriate oxonium salts were isolated which did not decompose by sublimation under reduced pressure or heating in aqueous solution to the original epoxides. It was proved by some analytical reactions (with silver nitrate, Berlin blue) that they split off hydrogen cyanide under the formation of the appropriate halogenoketones.

The stretching vibration of the $-\text{CN}$ group at 2250 cm^{-1} as well as bands belonging to $-\text{OH}$ group vibration at 3330 cm^{-1} were observed in the i.r. spectra of the oxonium salts. The best measuring was obtained in paraffin oil suspension. In chloroform solutions it was impossible to observe the vibration of the $-\text{CN}$ group similarly as with 1,3-epoxides. In KBr pellets also bands belonging to $\nu(\text{C}=\text{O})$ appeared beside the $-\text{CN}$ vibration. These salts were probably decomposed to halogenoketones during preparation of the pellets. Similar decomposition of oxonium salts was observed during determination of melting points, therefore, the determination in capillaries was more advantageous.

Bands belonging to the $n \rightarrow \pi^*$ transitions were not observed in the u.v. spectra of these salts similarly as in the case of the epoxides. We failed to interpret the $^1\text{H-n.m.r.}$ spectra.

In the i.r. spectra of halogenoketones, obtained by thermal decomposition, the bands belonging to $\nu(\text{CN})$ and $\nu(\text{OH})$ were not observed but characteristic bands of the $\nu(\text{C}=\text{O})$ groups appeared at 1740 cm^{-1} . In the $^1\text{H-n.m.r.}$ spectra of halogenoketones with the same halogen it was possible to find a singlet correspond-

ing to the proton in $-\text{CH}_2-$ groups of the cyclopentanone ring and a multiplet belonging to eight protons in $-\text{CH}_2\text{X}$. In the case of different halogens a multiplet was observed also in the $-\text{CH}_2-$ groups of the cyclopentanone ring. In the u.v. spectra of the halogenoketones the bands belonging to the $n \rightarrow \pi^*$ transitions (from 290 to 340 nm) were identified. In the mass spectrum of the halogenoketone V a molecular peak at m/e 322 as well as other ionic fragments were observed. The similarly accomplished reactions with 2,2,6,6-tetrakis(chloromethyl)cyclohexanone did not give similar results; the unchanged components were isolated [16].

On the basis of the obtained results it can be stated that the 1,3-epoxides, not described in the literature as yet, proved the formation of the epoxide structure not only in aliphatic but also in some cyclic halogenoketones. In this type of β -halogenoketones they were the only products in the reaction of the carbonyl group. That is, we found that the carbonyl group in this case did not afford oximes, phenylhydrazones, and cyanohydrins [16]. The starting THCP did not give the above-mentioned derivatives either [1, 17] and the authors of these papers ascribed this fact to sterical shielding of the carbonyl group.

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