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REACTIONS OF p-HYDROXYPHENYL- AND p-PHENOLATOTHIANIUM COMPOUNDS

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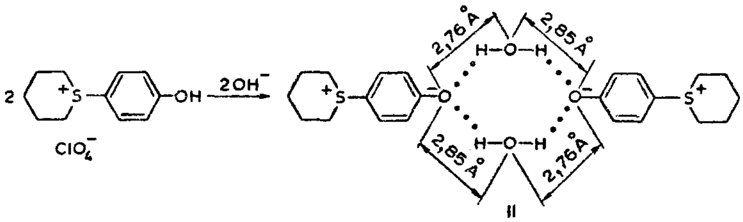
p-Hydroxyphenylthianium perchlorate reacts with OH^- to give bis(p-phenolatothianium) dihydrate, in which the oxygen atoms of the zwitter ions are tied up in an eight-membered ring by hydrogen bonds with the H_2O molecules. The unit cell of the perchlorate consists of two cations and two anions bonded by linear and forked hydrogen bonds. p-Hydroxyphenylthianium perchlorate reacts with a concentrated solution of KOH in methanol to give 1-(p-hydroxyphenyl)-1'-(p-phenolato)bisthianium perchlorate, which is also obtained by the reaction of p-hydroxyphenylthianium perchlorate with bis(p-phenolatothianium) dihydrate and of the latter with $HClO_4$. 1-(p-Hydroxyphenyl)-1'-(p-phenolato)bisthianium chloride hydrate and 1-(p-phenolato)thianiumbisphenol, respectively, were obtained by the reaction of bis(p-phenolatothianium) dihydrate with p-hydroxyphenylthianium chloride or with C_6H_5OH. Under the influence of picric or perchloric acid, 1-(p-h droxyphenyl)-1'-(p-phenolato)bisthianium perchlorate is converted to p-hydroxyphenylthianium picrate or its perchlorate, respectively, while reaction with OH^- gives bis(p-phenolatothianium) dihydrate, and heating with piperidine gives p-hhdroxyphenyl ω-piperidinoamyl sulfide. When bis(p-phenolatothianium) dihydrate is heated, it undergoes dehydration and polymerization to $[-OC_6H_4S(CH_2)_5-]_n$; depending on the conditions, n = 2, 3, 14, or 25. p-Hydroxyphenyl ω-piperidinoamyl sulfide is formed when II is heated with piperidine.

p-Hydroxyphenylthianium perchlorate (I) is converted to a base, viz., bis(p-phenolatothianium) dihydrate (II), when a soltuion of it in methanol, alcohol, or water is allowed to react with potassium hydroxide or when a methanol solution of I is treated with an anion-exchange resin (in the OH^- form):



II

This reaction is not a case of simple replacement of the anion, as assumed in [1], but rather involves proton transfer with the formation of p-phenolatothianium zwitter ions and water molecules that are bonded to them. According to data from x-ray diffraction analysis [2], the oxygen atom of the zwitter ion is tied up by hydrogen bonds simultaneously with two water molecules, which leads to the development of an eight-membered ring that is formed by four hydrogen bonds and four O–H bonds. The $O^-...O$ distance in two of the $O^-...H–O$ fragments

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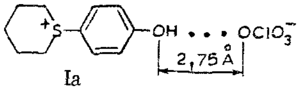
is 2.76 Å, and the O–H bond length is 0.93 Å, as compared with 2.85 and 0.72 Å, respectively, in the other two O^-...H–O fragments.

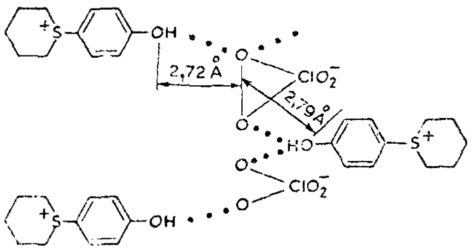
The broad absorption band at 2600-3500 cm^{-1} with two maxima at 3220 and 3330 cm^{-1} in the IR spectrum of II corresponds to associated OH groups. According to the correlation in [3], the O...O distances between the oxygen atoms tied up by a hydrogen bond that correspond to these maxima are 2.73-2.75 and 2.79-2.80 Å, while the energies of the H bonds calculated by the method in [4] with the aid of the frequencies of the same maxima are, respectively, 6.64 ± 0.10 and 5.66 ± 0.10 kcal/mole. Absorption bands are not observed at 3400 cm^{-1}, from which it follows that the water molecules in II do not form hydrogen bonds with one another.

Hydrogen bonds with an energy [4] of 5.6 ± 1.1 kcal/mole are also present in the crystals of starting salt I. It follows from the IR spectrum that the hydrogen bonds in this compound are formed with the participation of perchlorate anions, as evidenced by the broad bands at 1100 cm^{-1}. Absorption bands of a free hydroxy group are not observed, but the spectrum does contain a slightly unsymmetrical absorption band with a maximum at 3280 cm^{-1}, which is characteristic for an OH group involved in a hydrogen bond. According to the correlation in [3], in salt I the distance between the oxygen atoms involved in hydrogen bonding is 2.73 Å. This value virtually coincides with the value obtained from an x-ray determination of this distance for structure Ia, which is 2.75 Å.

According to the data from x-ray diffraction analysis [5], the unit cell of salt I consists of two $p\text{-}HOC_6H_4S^+$ cations and two ClO_4^- anions. The cations are bonded with the anions by hydrogen bonds of two types, viz., almost linear bonds and forked bonds (structures Ia and Ib, respectively):



Ia

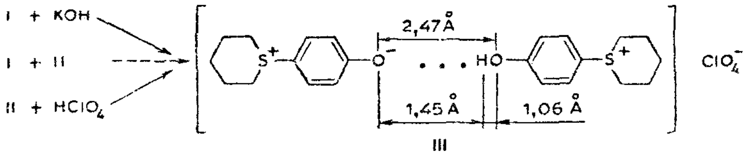


Ib

Structure Ia involves ion pairs of cations and anions, while structure Ib involves infinite chains joining pairs of cations and anions. The crystal of salt I is made up of alternating structures Ia and Ib. According to the results of x-ray diffraction analysis, the distances between the oxygen atoms that participate in the hydrogen bonds are 2.75 Å for Ia and 2.72 and 2.79 Å, alternately, for Ib. The O...O distances of the forked hydrogen bond in Ib cannot be calculated from the IR spectrum because of the absence of correlation data.

A bissulfonium salt, viz., 1-(p-hydroxyphenyl)-1'-(p-phenolato)bisthianium perchlorate (III), is formed in addition to II in the reaction of methanol solutions of salt I with potassium hydroxide. Compound II was obtained in optimal yield in dilute solutions and at concentrations on the order of 0.5 mole/liter [1]. Primarily III is formed in concentrated solutions at concentrations of no less than 0.2 mole/liter; excess perchlorate I favors the formation of III.

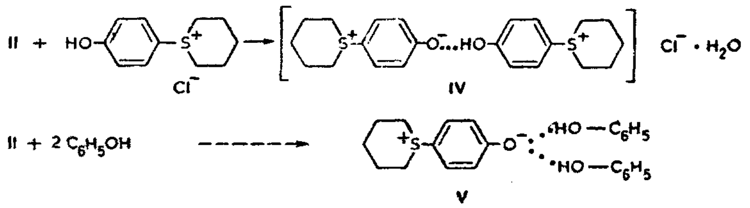
Bissulfonium salt III is also obtained by the reaction of base II with perchlorate I or by the action of a stoichiometric amount of perchloric acid on base II:



III

According to the IR spectrum and the results of x-ray diffraction analysis [6], crystalline bissulfonium salt III is constructed with the participation of hydrogen bonds. The band of stretching vibrations of the OH group in the IR spectrum of this salt is broadened considerably and shifted to low frequencies; the center of gravity of the band is found at ~1200 cm^{-1}, and the corresponding distance between the oxygen atoms that participate in the hydrogen bonding is, according to [3], 2.4 Å. According to the x-ray diffraction data [6], it is 2.471(7) Å, while the distances between the oxygen atoms and the proton are, respectively, 1.45(9) and 1.06(9) Å. In contrast to starting salt I, the perchlorate anion in bissulfonium salt III does not participate in hydrogen bonding. According to the results of x-ray diffraction analysis, it has an undistorted tetrahedral configuration. This is responsible for the presence in the IR spectrum of a narrow absorption band at 1100 cm^{-1} (a weakly resolved doublet). According to the equation in [4], the energy of formation of the hydrogen bond in salt III is three times the value in salt I and amounts to 15.8 ± 0.5 kcal/mole.

Salts that involve the participation of a zwitter ion, viz., 1-(p-hydroxyphenyl)-1'-(p-phenolato)bisthianium chloride hydrate (IV) and 1-(p-phenolato)thianiumbisphenol (V), are obtained from base II and p-hydroxyphenylthianium chloride or phenol:

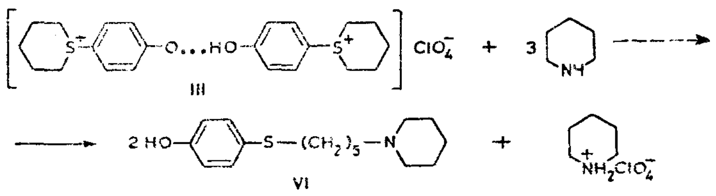


A water band at 3400 cm^{-1} is observed in the IR spectrum of bissulfonium salt IV (which is a hydrate). In other respects the sections of the IR spectra of salts III and IV in the region of the stretching vibrations of the OH group are identical, on the basis of which it may be concluded that the hydrogen bond in IV participates in the formation of a complex cation; the chloride ion does not participate in the hydrogen bond with the cation. The energy of the hydrogen bond in hydrate IV is 15.8 ± 0.5 kcal/mole.

Judging from the IR spectrum, the OH groups in V are associated, and both phenolic hydroxy groups are probably tied up with the oxygen atom of the phenolatothianium by means of hydrogen bonds.

The complex cations of the bissulfonium salts are decomposed by the action of both acids and bases. Under the influence of picric or perchloric acid, bissulfonium salt III is converted in quantitative yield to p-hydroxyphenylthianium picrate or perchlorate (I), respectively. Base II is formed in quantitative yield when a solution of salt III is passed through an anion-exchange resin (in the OH form), and a similar transformation occurs when salt III is heated with a solution of potassium hydroxide in methanol.

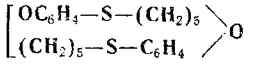
When salt III is heated with piperidine, both cationic fragments undergo reaction to give p-hydroxyphenyl-ω-piperidinoamyl sulfide (VI), as we have previously described [7] for perchlorate I:



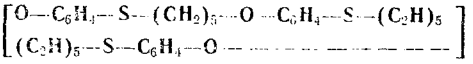
The zwitter ion in II-V is stabilized due to the formation of ionic-ionic (I, III, and IV) or ionic-molecular (II and V) hydrogen bonds. The unstabilized phenolatothianium molecule is unstable. At 141-143°C bis(p-phenolatothianium) dihydrate II rapidly splits out water; according to data from thermographic analysis, the weight loss ranges around 10%. As a result of attack by a nucleophile, viz., another phenolatothianium molecule, the free p-phenolatothianium molecule undergoes cleavage at the C–S bond to give a polymeric chain. An oligomer with mp 121-123°C is formed. According to the data from the IR spectrum, the sulfur in the oligomer is incorporated in the composition of the C–S–C grouping: absorption bands with frequencies that are characteristic for sulfide sulfur are observed [1]; the average molecular weight corresponds to n = 14:

$$n\text{II} \xrightarrow{143^\circ} 2\left[\text{O}-\text{C}_6\text{H}_4-\text{S}-(\text{CH}_2)_5\right]_n + 2n\,\text{H}_2\text{O}$$

The oligomer is insoluble in water and polar solvents but dissolves when it is heated in benzene and piperidine. Small amounts (no more than 10%) of oligomers with mp 118-121°C are formed during prolonged storage of base II. When a solution of II in pentanol is refluxed, i.e., when it is heated at a temperature close to the dehydration threshold, a mixture of oligomers with n ≥ 2 is formed. The character of the reaction of hydrated phenolatothianium molecule II with amines entails conditions for the formation of a free zwitter ion: If the boiling point of the amine is lower than the dehydration threshold of the zwitter ion, amino sulfide VI is formed. Thus, VI is formed almost exclusively in piperidine (the reaction proceeds considerably more slowly than with perchlorate I [7]). Only an oligomer with n = 25 is obtained with dibutylamine, which boils above the dehydration threshold, i.e., the rate of polymerization under these conditions considerably exceeds the rates of the reactions of both base II and the free zwitter ion with dibutylamine. A mixture of heterochain dimers and trimers is formed when base II is heated with a mixture of dibutylamine and pentanol. Absorption bands of OH groups are not observed in the IR spectra of these oligomers; they are evidently macrocycles:



$$\left[\begin{array}{l}\text{OC}_6\text{H}_4-\text{S}-(\text{CH}_2)_5\\(\text{CH}_2)_5-\text{S}-\text{C}_6\text{H}_4\end{array}\right.\!\!\!>\text{O}$$



$$\left[\begin{array}{l}\text{O}-\text{C}_6\text{H}_4-\text{S}-(\text{CH}_2)_5-\text{O}-\text{C}_6\text{H}_4-\text{S}-(\text{C}_2\text{H})_5\\(\text{C}_2\text{H})_5-\text{S}-\text{C}_6\text{H}_4-\text{O}-\text{---------}\end{array}\right]$$

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil and hexachlorobutadiene were obtained with a UR-20 spectrometer.

Bis(p-phenolatothianium) Dihydrate (II). A solution of 0.53 g (1.8 mmole) of perchlorate I [8] in methanol was percolated through a column filled with AB-17 anion-exchange resin in the OH form and eluted exhaustively with methanol. Dihydrate II was obtained in quantitative yield and was identical to II obtained by the method in [1] with respect to its decomposition temperature and IR spectrum.

1-(p-Hydroxyphenyl)-1'-(p-phenolato)bisthianium Perchlorate (III). A. From I and II. A solution of 1.11 g (5.2 mmole) of dihydrate II in 6 ml of methanol (a 15% solution, 0.87 mmole/liter) was added to a solution of 1.54 g (5.2 mmole) of I in 6.5 ml of methanol (a 19% solution, 0.8 mmole/liter). The reaction mixture solidified to a white crystalline mass, which was heated to the boiling point, cooled, and filtered to give 2.27 g (87%) of III with mp 185-186°C (from water).* Found: C 53.9; H 6.0; Cl 7.4%. $C_{22}H_{29}ClO_6S_2$. Calculated: C 54.0; H 5.9; Cl 7.3%. The S^+ content in the zwitter ion was found by the method in [9] to be 6.55% (as compared with the calculated value of 6.55%). The solubilities of perchlorate III in various solvents at 20°C were as follows: 1.3% in methanol, 0.4% in alcohol, 0.07% in acetone, and 1.7% in water. The mass spectrum of III did not contain a molecular-ion peak but did contain a peak with m/e 388 (M − $HClO_4$).

B. From Dihydrate II and Perchloric Acid. A 0.56-g (2.3 mmole) sample of 42% perchloric acid was added dropwise to a solution of 1.0 g (4.7 mmole) of dihydrate II in 5 ml of alcohol (0.94 mole/liter). Workup gave perchlorate III in 81% yield; workup of the mother liquor gave another 10.3% of III with mp 176-176.5°C.* Found: C 54.3; H 5.7%. $C_{22}H_{29}ClO_6S_2$. Calculated: C 54.1; H 5.9%.

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*Perchlorate III crystallized from methanol or alcohol to give a product with mp 176-176.5°C, whereas it crystallized from water to give a product with mp 185-186°C. The IR spectra of the crystallized products were identical, and the low-melting sample was subjected to x-ray diffraction analysis [5].

C. From Perchlorate I and Potassium Hydroxide. A solution of 8.71 g (29 mmole) of perchlorate I in 47 ml of methanol (0.63 mole/liter) was added to a solution of 1.66 g (29 mmole) of potassium hydroxide in 36 ml of methanol (0.8 mole/liter). After 12 h, the potassium perchlorate was removed by filtration, and the filtrate was concentrated, as a result of which, III precipitated in 56% overall yield. Workup of the mother liquor gave II in 30% yield. In another experiment a solution of 15 mmole (0.84 g, a 100% excess) of potassium hydroxide (2.5 moles/liter) was added to a solution of 4.42 g (15 mmole) of perchlorate I in 70 ml of water (0.21 mole/liter). Workup gave 36% III containing a small amount of potassium perchlorate, for the separation of which the product was dissolved by heating in methanol. Another 3% of III and 63% of base II were isolated from the filtrate of the reaction mixture.

Reaction of Perchlorate III with Acids. A. With Perchloric Acid. A 0.13-g (0.53 mmole) sample of 42% perchloric acid was added to a suspension of 0.26 g (0.53 mmole) of III in 3 ml of aqueous alcohol (1:1), during which a clear solution formed immediately. The solvents were evaporated *in vacuo* with gentle heating. The yield of perchlorate I was 0.22 g (71%). The reaction product was washed with ether to remove traces of acid to give a product with mp 143-144°C. No melting-point depression was observed for a mixture of this product with a genuine sample.

B. With Picric Acid. A solution of 0.3 g (0.61 mmole) of III in 31 ml of alcohol was added to 6 ml (1.3 mmole) of a 5% alcohol solution of picric acid. After 15 min, crystals of 1-(p-hydroxyphenyl)thianium picrate, with mp 200-201.2°C, precipitated in quantitative yield. No melting-point depression was observed for a mixture of this product with a genuine sample. Found: C 48.5; H 4.2; N 9.9; S 7.1%. $C_{17}H_{17}O_8N_3S$. Calculated: C 49.3; H 4.0; N 9.9; S 7.6%.

Reaction of Perchlorate III with Bases. A. Treatment with an Anion-Exchange Resin. A solution of 0.24 g (0.5 mmole) of III in 20 ml of absolute methanol was percolated through a column filled with 2 ml of AB-17 anion-exchange resin in the OH form, and the solvent was evaporated from the desorbate *in vacuo* without heating. The residue was recrystallized from methanol with ether to give 0.17 g (81%) of dihydrate II with mp 147-150°C (dec.). Found: S^+ 14.6%. $C_{11}H_{16}O_2S$. Calculated: S^+ 15.1%. The IR spectrum was identical to the spectrum of genuine II.

B. Reaction with Potassium Hydroxide. A hot solution of 3.99 g (8.2 mmole) of III in 95 ml of methanol was added to a solution of 0.46 g (8.2 mmole) of potassium hydroxide in 4 ml of methanol, and the mixture was refluxed for 3.5 h. It was then cooled, and the potassium perchlorate was removed by filtration. The filtrate was concentrated to half its original volume, and the concentrate was refluxed for another 4.5 h. It was then concentrated to one third of its original volume and cooled to separate III (0.19 g was recovered). The solvent was removed from the filtrate by distillation, and the residue was diluted with acetone and ether to precipitate 2.06 g of dihydrate II. Another 0.91 g of II was precipitated from the mother liquor by the addition of acetone. The overall yield was 86%, and 6% of the III was recovered.

C. With Piperidine. A mixture of 20 ml of piperidine and 2.05 g of perchlorate III was refluxed for 4 h, after which the excess piperidine was removed by distillation. The VI was extracted with benzene and washed with acetone. The yield of product with mp 116-117°C [7] was 1.39 g. The residue from the reaction mixture was then washed with water to remove the piperidine perchlorate [0.73 g (94%)], and another 0.48 g of VI was isolated from the residue after treatment with water; the overall yield was 79.5%.

1-(p-Hydroxyphenyl)-1'-(p-phenolato)bisthianium Chloride Hydrate (IV). A solution of 0.59 g (2.78 mmole) of II in 4.5 ml of methanol (0.61 mole/liter) was added to a solution of 0.6 g (2.4 mmole) of 1-(p-hydroxyphenyl)thianium chloride [8] in 4.5 ml of methanol (0.53 mole/liter). After 12 h, the solvent was evaporated *in vacuo*, and the residue was washed with ether to give 0.90 g (84.8%) of IV with mp 112-115°C. Found: C 59.3; H 7.0; Cl 7.9; ionic Cl 8.4; total sulfonium S^+ 15.2; sulfonium S^+ in the zwitter ion [9] 6.9%. $C_{22}H_{29}ClO_2S_2 \cdot H_2O$. Calculated: C 59.7; H 7.0; Cl 8.0; total sulfonium S^+ 14.4; sulfonium S^+ in the zwitter ion 7.2%.

1-(p-Phenolato)thianiumbisphenol (V). A solution of 1.06 g (5 mmole) of II in 10 ml of methanol was added to a solution of 1.41 g (15 mmole) of phenol in 1.5 ml of methanol. After 12 h, the solvent was removed by vacuum distillation, and the excess phenol was extracted from the residue with ether. The reaction product was washed to remove the phenol and recrystallized from acetone to give 1.2 g (63%) of a product with mp 118-119°C. Found: C 72.9; H 6.9; S 8.1; zwitter ion S^+ [9] 8.3%. $C_{23}H_{26}O_3S$. Calculated; C 72.3; H 6.8; S 8.4%.

Conversion of Dihydrate II by Heating. A. A 0.77-g (3.6 mmole) sample of dihydrate II was heated at 151°C, during which vigorous foaming and the liberation of water were observed (the water was absorbed with silica gel impregnated with cobalt salts). When II was heated with a derivatograph, decomposition commenced at 141°C, and the weight loss was 10% (as compared with a calculated value of 8.5%). The product had mp 121.5-123°C. The solubility in the case of heating in benzene was 3.5%, and the product was not volatile at 260°C (10^{-8} mm). Found: C 67.2; H 7.1; S 16.5%. $C_{11}H_{14}OS$. Calculated: C 68.0; H 7.2; S 16.5%. M* 2844 ± 6.5; 2586 ± 12 [for $(C_{11}H_{14}OS)_n$ n = 14.66; 13.33].

B. A 10-ml sample of pentanol was added to 0.30 g (1.48 mmole) of II, and the mixture was refluxed for 2.5 h. When the mixture was cooled, a solidified melt formed on the bottom, and a suspension of flakes formed above it. The suspension was separated and washed with acetone and ether to give 0.12 g of a product with mp 149-149.5°C and M 486 ± 2 [n = 2.51 for $(C_{11}H_{14}OS)_n$]. The solidified melt (0.08 g) had mp 124-149°C (146-148.5°C after cooling) and M 708 ± 3 (n = 3.65). The overall yield of oligomers was 73%.

C. A mixture of 0.40 g (1.89 mmole) of II and 8 ml of di-n-butylamine was heated with stirring at 158-159°C for 4 h, during which water was liberated, and the mixture separated into layers. An oligomer precipitated when the mixture was cooled. The yield of product with mp 117-120°C and M 4944 ± 23 [n = 25.5 for $(C_{11}H_{14}OS)_n$] was 0.22 g (60%).

D. A solution of 0.40 g (1.89 mmole) of II in a mixture of 6 ml of pentanol and 0.49 g (3.8 mmole) of di-n-butylamine was refluxed for 2 h (the temperatre in the mixture was 137-138°C), after which it was cooled, and the precipitated oligomer was removed by filtration to give 0.27 g (74%) of a product with mp 148.5-150°C. Found: C 68.1; H 7.2%. $C_{11}H_{14}OS$. Calculated: C 68.0; H 7.2%. Found: M 513 ± 2; 506 ± 2 [for $(C_{11}H_{14}OS)_n$ n = 2.64; 2.61].

Reaction of Base II with Piperidine. A. A mixture of 0.54 g (2.55 mmole) of base II, 0.44 g (5.17 mmole) of piperidine, and 11 ml of alcohol was refluxed for 2 h, after which the solvents were removed by distillation, and amino sulfide VI was extracted from the residue with ether. The amino sulfide was converted to the hydrochloride (8.5%) [7] with mp 166-168°C. No melting-point depression was observed for a mixture of this product with a genuine sample. A total of 80% of II was recovered.

B. A 0.44-g (2 mmole) sample of II was refluxed with 10 ml of piperidine for 1 h, and the mixture was worked up to give 17.3% of amino sulfide VI (isolated in the form of the hydrochloride). A total of 64% of II was recovered.

C. A 0.28-g (1.3 mmole) sample of base II was refluxed with 10 ml of piperidine for 6 h, after which the piperidine was removed by distillation, and amino sulfide VI was extracted from the residue with ether and converted to the hydrochloride (70%) [7].

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*Here and below — ebulliometry in benzol.