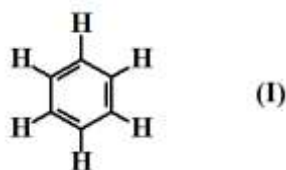


Cyclohexatriene Benzene Structure

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Abstract: Впервые синтезированы орто-изомерные вещества: 1-гидрокси-2-тио-4-трет.-бутилциклогексаatriен-2,4,6 и 1-гидрокси-2-тио-4-трет.-бутилциклогексаatriен-1,3,5 что свидетельствует о наличии в молекуле бензола трех простых и трех двойных связей. Характер простых и двойных связей проявляется с введением в молекулу бензола какого-нибудь радикала. Таким образом, гипотеза великого немецкого ученого Августа Кекуле о циклогексаatriеновой структуре бензола, выдвинутая им в 1865 году, нашла свое экспериментальное подтверждение. Синтез орто-изомерных веществ. Синтез орто-изомерных веществ, также показывает необоснованность теорий резонанса и суперпозиции Лайнуса Полинга. Перед учеными открываются широкие возможности синтезировать предложенным способом и исследовать многочисленные орто- и мета-производные бензола.

Keywords: benzol,kekule,formula,meyer It is known that August Kekule suggested a cyclohexatriene formula for benzene(I) in 1865 [1-5]:

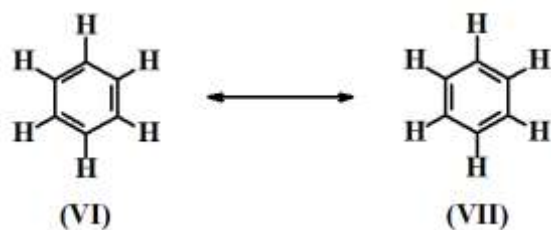


But Ladenburg (1869) pointed out that a cyclohexatriene formula presupposes a greater number of disubstituted products than actually existed [2]. In fact, if it is being based on fatty chemistry, disubstituted benzenederivatives should have two ortho- (II, III) and two meta- (IV, V) isomers:



In connection with this Meyer (1870) supposed that the distinction between those isomers might be too little to be discovered [2].

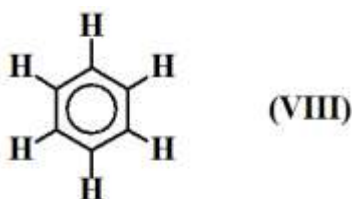
In order to preserve his suggested formula and to explain the absence of the second isomers, Kekule had to put forward a special hypothesis on "oscillation" of bounds [1-5]:



But such simple solution of the problem could not satisfy everybody and in 1904 Harries proved the existence of three stable double bonds in benzene molecule by means of experiments [2].

Another theoretical basis of cyclohexatrienebenzene formula might be the theory of color value (by O. Vitt) which have been known since 1876 and which plays an important role in chemical composition determining of organic substances. Because products of benzene serve as the basis for colorants that directly proves the existence of CH=CH chromophore in benzene molecule.

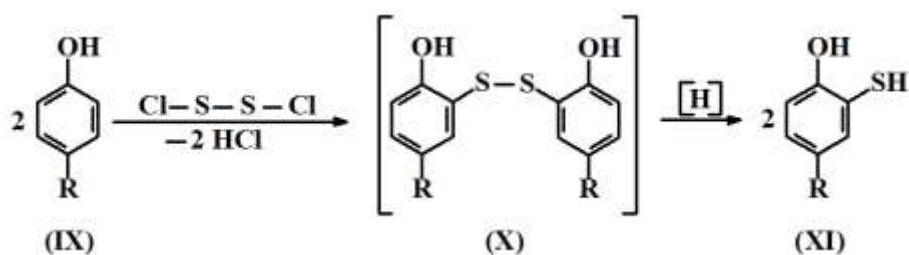
In spite of practical and theoretical presuppositions, the researchers couldn't experimentally prove the existence of isomers at disubstituted benzene (II, III, IV, V). Probably just for this reason they not only had to agree with Kekule but also tried to "develop" the "oscillation" theory. As a result the false direction of "the resonance theory" (VIII) (Linus Pauling, 1928) appeared. In spite of its 80 year dominance "the resonance theory" remains just scientific hypothesis now. It is quite naturally that this theory will never be proved in an experimental way:



The data of X-ray structural analysis on which L. Pauling based, show that all six bonds in benzene are equal and have the length of 1,39 Å, that is, they are intermediate in their length between the single and the double bonds [3]. It must be like this. It is enough to understand that equal bond length is conditioned by the cyclic nature of a benzene molecule, it means that the whole cycle length is distributed among the bonds equally, despite the fact, whether they are single or double. Finally the equal distance between the carbonic atoms does not mean that the disubstituted products of benzene have no isomers (II, III, IV, V).

Evidently the main point of the resonance theory is "to explain" the reason of isomers' absence of the disubstituted benzene products. In other words, the only way of solving the problem is the synthesis of ortho- (II, III) and meta- (IV, V) substances of disubstituted products.

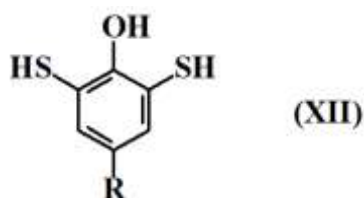
In 1976 A. Kuliyeu with his colleges showed the reduction of disulfide (X) during interaction of p-alkylphenol with monochloride sulphur [6]:



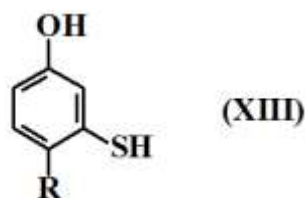
In the process of reduction 1-hydroxy-2-thio-4-alkylbenzene (XI) with yield amounted to 31,3% was synthesized and analysed. But the other product with much bigger yield amounted to 68,7% had not been studied and there was no any information about it. Besides this, the fact of hydrogen sulphide isolation in the process of sulphide mass (X) reduction was not explained. The most important thing is that there is no information concerning the splitting of chromophore of colourful sulphide mass (X).

All mentioned above refer to the chemical composition and structure of substances, which were mistakenly accepted in the literature as sulphur monochloride (S_2Cl_2) [7-9]. The following important remarks pointed below were not described in the article of A. Kuliyeu and colleagues [6]:

Firstly, according to the resonance theory when p-alkylphenol interacts with sulphurmonochloride (4:1) as the result polysulfide is generated. And in the reduction of polysulfide along with substance (XI) 1-hydroxy-2,6-dithio-4-alkylbenzene (XII) must be synthesized:



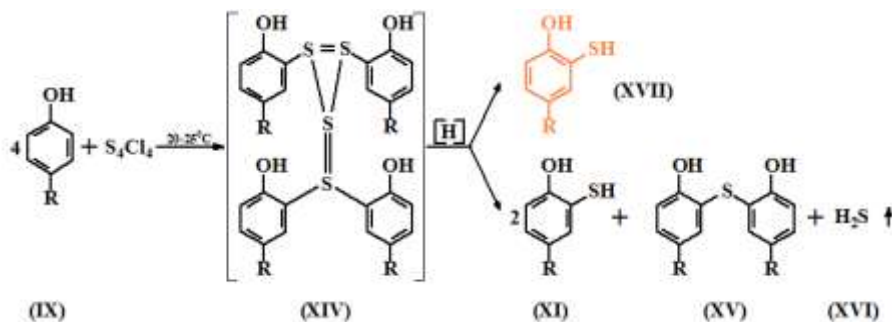
Secondly, according to the resonance theory 1-hydroxy-3-thio-4-alkylbenzene (XIII) must be also generated as a result of interaction of p-alkylphenol and sulphurmonochloride (4:1):



Thirdly, according to the same resonance theory substance synthesized by A. Kuliyeu and colleagues (XI) must be coloured as it carries not only ($\text{CH}=\text{CH}$) chromophore group but also ($\text{OH}-$; $\text{SH}-$) auxochrome group.

The scientific hypotheses and practical investigations mentioned above induced us to study the problem concerning cyclohexatrienebenzene structure more thoroughly.

Our investigations showed that disubstituted benzene ortho-derivatives actually have two isomers. *p*-tert-butylphenol is subjected to the reaction with sulphur chloride (S_4Cl_4) (4:1) and at the temperature 20-25°C is conducted according to the reaction scheme given below. In the process of reduction along with the first isomer 1-hydroxy-2-thio-4-tert.-butylcyclohexatriene-2,4,6, (**XI**) and with the compound 2-thio-bis-(1-hydroxy-4-tert.-butylcyclohexatriene-2,4,6) (**XV**), the second isomer 1-hydroxy-2-thio-4-tert.-butylcyclohexatriene-1,3,5 (**XVII**) of yellow colour with yield of $\approx 0,5\%$ is generated (table) [7-9]:

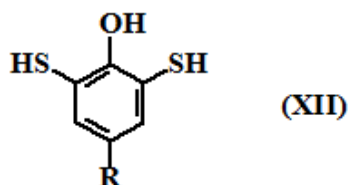


According to the resonance theory the equal reaction capability of hydrogen atoms being in positions 2 and 6 relative to a hydroxyl group, sulphidation of *p*-alkylphenols should have resulted in polysulphides generation.

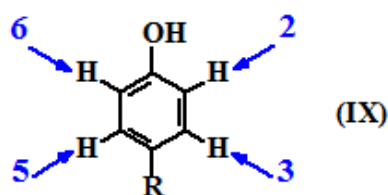
Table: Compounds synthesized by reacting *p*-alkylphenol and sulphur monochloride and reducing tetrasulphide

p-alkyl phenol: sulphur monochloride ratio	Temperature, °C	Substance yield, %				
		XI	XV	XII	XVI	XVII
					H_2S	
4:1	20-25	49	44,5	-	4,6	$\approx 0,5$

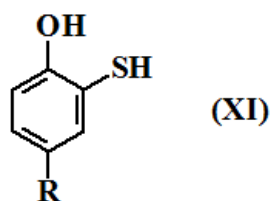
However, we have not discovered polysulphides in the products of *p*-alkylphenol sulphidation. The reduction of sulphide mass, as it was pointed above, results in obtaining three products: 1-hydroxy-2-thio-4-tert.-butylcyclohexatriene-2,4,6 (**XI**), 2-thio-bis-(1-hydroxy-4-tert.-butylcyclohexatriene-2,4,6) (**XV**) and 1-hydroxy-2-thio-4-tert.-butylcyclohexatriene-1,3,5 (**XVII**). 1-hydroxy-2,6-dithio-4-tert.-butylcyclohexatriene (**XII**) has not been discovered in the reduction products (**XIV**), nevertheless it must have been produced according to the resonance theory, under the equal reaction ability of hydrogen atoms in positions 2 and 6:



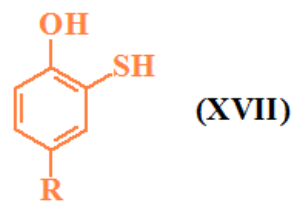
The fact that 1-hydroxy-3-thio-4-alkylbenzol (XIII) and 1-hydroxy-2,6-dithio-4-tret.-butylcyclohexatriene (XII) have not been produced in the process of reducing sulphide mass (XIV) is absolutely natural and confirms that the 2nd, the 3rd, the 5th and the 6th hydrogen atoms in p-alkylphenol molecule are different in electron density. And this proves the existence of single and double bounds in p-alkylphenol molecule.



The difference of hydrogen atoms in electron density and reactionary capacity results in that more than 99,5 % of chlorine atoms (Cl^Γ) “attack”, in the first place, the hydrogen that is adjacent to the single bond (relative to OH) and the first ortho-isomer 1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-2,4,6 (XI) and 2-thio-bis-(1-hydroxy-4-tret.-butylcyclohexatriene-2,4,6 (XV) are produced in the process of reduction. Only ≈ 0,5% of chlorine atoms “attack” the hydrogen that is adjacent to the double bond (relative to OH), which process results in producing the second ortho-isomer: 1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-1,3,5 (XVII). These isomers are different in colour, boiling point and refraction. The absence of colour in the first isomer (XI) and the existence of it in the second one (XVII) are directly connected with their structure and comply with **the theory of colour value** requirements.



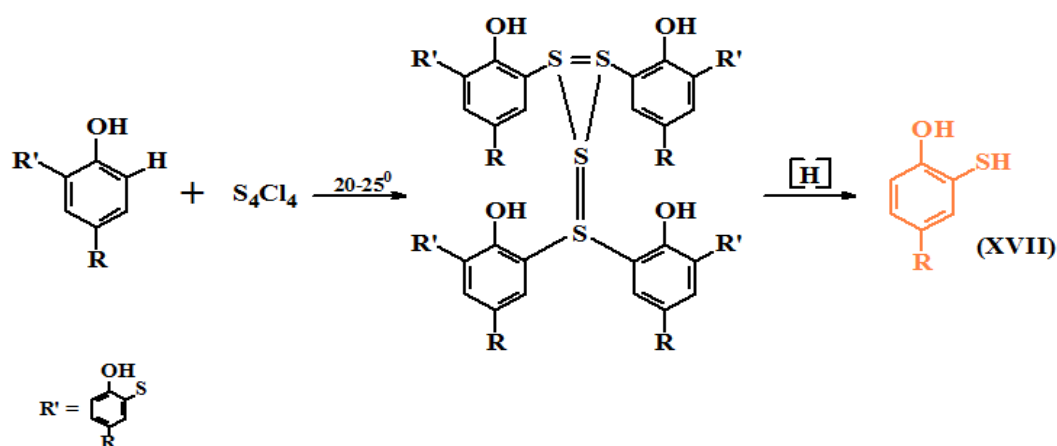
colourless substance
1-hydroxy-2-thio-4-tret.-
butylcyclohexatriene-2,4,6 (XI)



yellow coloured substance
1-hydroxy-2-thio-4-tret.-
butylcyclohexatriene-1,3,5 (XVII)

The colour distinction of both substances with the same composition verifies the cyclohexatriene structure of benzene. The compound (XI), conditionally called as the “first” isomer, is colourless, as the auxochrome groups are adjacent to the single bond (CH–CH). And these condimer (XVII) is coloured as the auxochrome groups are adjacent to the double bond, i.e. to the chromophore bond (CH=CH). Therefore, the compound synthesized by A. Kuliyeve and colleagues (XI) is colourless.

In order to synthesize the “second” isomer (**XVII**), it means the coloured one, it is necessary to substitute the hydrogen atom, which is adjacent to the single bond (relative to OH), by some radical. In that case the chlorine (Cl) being a nucleophilic agent, will be forced to “attack” the hydrogen being adjacent to the double bond (relative to OH). To carry out such reaction we used 2-thio-bis-(1-hydroxy-4-tret.-butylcyclohexatriene-2,4,6) (**XV**) [7-9]. The reaction is preceded by the following scheme:



In the process of reduction the second yellow coloured orthoisomer 1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-1,3,5 (**XVII**) was produced with a yield of 18% [7,8] (the rest product with the 82% yield has not been investigated yet).

Experimental part

Synthesis of 1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-2,4,6 (XI), 1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-1,3,5 (XVII) and 2-thio-bis-(1-hydroxy-4-tret.-butylcyclohexatriene-2,4,6) (XV)

150g of p-tret.-butylphenol solution was dissolved in 300 ml. of benzene and then 67,5g of sulphur monochloride was dropwise added to it during 60 minutes at a reaction temperature of 20-25°C. The reaction mixture was mixed during 40-60 minutes at a temperature of 70-75°C. Then the tetrasulphide mass was reduced by atomic hydrogen (Zn+HCl) during 24 hours at a temperature of 10-20°C. The reduction process was conducted until the chromophore groups became completely splitted. The obtained mass was washed sequentially with hot water. Then the benzene was distilled. The residue part was distilled in vacuum and the following substances were synthesized:

1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-2,4,6 (**XI**), as a colourless liquid with the boiling temperature of 85-86°C (0,3mm) was obtained; d_4^{20} 1.0740; n_D^{20} 1.5590; $M_{r,54.79}$. Calc.: 54.86. Found out %: C 65.67; H 7.85; S 17.65. $C_{10}H_{14}OS$. Calculated %: C 65.89; H 7.73; S 17.59. Yield: 99,5%.

1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-1,3,5 (**XVII**), as a yellow liquid with the boiling temperature of 87-88°C (0,3mm) was obtained; n_D^{20} 1.5610; Yield: 0,5%.

2-thio-bis-(1-hydroxy-4-tret.-butylcyclohexatriene-2,4,6) (**XV**) was obtained as white crystals. The obtained substance was recrystallized from isooctane. The melting point: 92°C.

Synthesis of 1-hydroxy-2-thio-4-tret-butylcyclohexatriene-1,3,5 (XVII)

165g of 2-thio-bis-(1-hydroxy-4-tret.-butylcyclohexatriene-2,4,6) solution was dissolved in 300 ml of benzene and then 135g of sulphur monochloride was dropwise added at a reaction temperature of 20-25°C. The reaction mixture was mixed during 40-60 minutes at a temperature of 70-75°C. Then the sulphide mass was reduced by atomic hydrogen (Zn+HCl) during 24 hours at a temperature of 10-20°C. The mass obtained was washed sequentially with hot water. Then the benzene was distilled. The residue was distilled in vacuum and substance as a yellow liquid with the boiling temperature of 87-88°C (0,3mm) was obtained.
 n_d^{20} 1.5610. Yield: 18 %.

References

- [1]. А.Н.Несмеянов, Н.А.Несмеянов, "Начало орг.химии", том II, с. 10, Москва (1974);
- [2]. Л.Физер, М.Физер, "Орг.химия", том II, с.116-130, Москва (1970);
- [3]. Р.Моррисон, Р.Бойд, "Орг.химия.", с.301-303, Москва (1974);
- [4]. Дж.Робертс, М.Касерио. "Основа орг.хим.", том II, с.115-116, Москва (1968);
- [5]. М.Фримантл, "Химия в действии", том II, с.390, Москва (1991);
- [6]. А.Кулиев, Ш.Алиев, Ф.Мамедов, М.Мовсумзаде, ЖОрХ, том XII, вып.2, с.426, (1976);
- [7]. А.Зейналов, И.Асланов, А.Алиев, ЖВХО, 3, с.346, (1987);
- [8]. А.Зейналов. Диссерт. работа докт. хим. наук (1992);
- [9]. Р.Д.Абдуллаев, В.Н.Мамедов, Ш.А.Амиров, Л.А.Зейналова, «Сборник Известий» № 23, НАН Азерб. Респ., с.24-28 (2006).

Synthesis of ortho-isomeric substances:

**1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-2,4,6 and
1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-1,3,5**