

БРОМИРОВАНИЕ АРОМАТИЧЕСКИХ АМИНОВ**Ф.А. Мустафаева, Н.Т. Кахраманов**

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Учитывая, что антипирены, биологически активные вещества (противоопухолевые, антибактериальные, противогрибковые, противовирусные), фармакологические препараты, полученные, в частности, на основе бромсодержащих ароматических соединений, широко используются в промышленности и пользуются повышенным спросом, целью данной работы являлось обобщение и систематизация накопленных в этой области знаний. В статье были представлены методы, а также системы реагентов, используемые при бромировании ароматических аминов. Представлено бромирование ароматических аминов агентами галогенирования - бромистым водородом, бромидом натрия, бромидом калия, бромидом аммония, бромидом меди (II), N-бромсукцинимидом, N-бромсахарином, поддерживаемыми полимерами, и различия этих методов с точки зрения используемого окислителя, среды и растворителя, катализатора, региоселективности, количества атомов брома в полученном продукте. Показано влияние растворителей, катализаторов, природы (электронодонорной или электроноакцепторной) и положения (орто-, мета-, пара-) заместителей в ароматическом кольце, условий реакции, молярного соотношения реагентов, температуры реакции и времени проведения реакции бромирования ароматических аминов. Описаны направления реакций бромирования ароматических аминов в различных растворителях, в условиях отсутствия растворителей, в твердых состояниях. Изучено бромирование ароматических аминов в условиях термического, микроволнового, ультрафиолетового излучения. В статье показано региоселективное монобромирование, и также получение ди-, трибромпроизводных ароматических аминов. Также отмечены некоторые экологически безопасные методы бромирования ароматических аминов. Учитывая вышеуказанное, по нашему мнению, данные, представленные в этой статье, будут способствовать оптимизации получения бромпроизводных ароматических аминов, применяемых в промышленности, технике и технологии.

Ключевые слова: ароматические амины, анилины, бромирование, оксидбромирование, монобромирование, окислитель, галогенирующий агент, "in situ", региоселективность, катализатор

BROMINATION OF AROMATIC AMINES**F.A. Mustafayeva, N.T. Kakhramanov**

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It is known that the antipyrenes, biological active substances (antitumor, antibacterial, antifungal, antiviral), pharmacological preparations on the basis of bromine-containing aromatic compounds are widely used in the industry. Considering this and increased demand for these substances the purpose of this work was to summarize and systematize the accumulated knowledge in this area. The article presents methods and reagent systems used in the bromination of aromatic

amines. There have been described the bromination of aromatic amines with hydrogen bromide, sodium bromide, potassium bromide, ammonium bromide, copper (II) bromide, N-bromosuccinimide, N-bromosaccharin, polymer-supported halogenation agents, and difference of these methods from the point of view of the used oxidizer, the medium and the solvent, the catalyst, the regioselectivity, the quantity of bromine atoms in the obtained product. The influence of solvents, catalysts, the nature (electron-donor or electron-acceptor) and position (ortho-, meta-, para-) of the substituents in the aromatic ring, reaction conditions, molar ratio of the reagents, reaction temperature and carrying out time of bromination reaction of aromatic amines has been shown. The bromination reactions courses of aromatic amines in different solvents, in solvent free conditions, in solid states has been described. The bromination of aromatic amines under thermal, microwave, ultraviolet radiation conditions has been studied. In the paper the regioselective monobromination and also obtaining of di-, tri- bromo derivatives of aromatic amines has been shown. Taking into account today's priority to environmentally safe methods of bromination of aromatic amines they have been also mentioned. Given the above, in our opinion, the information presented in this article will help to optimize the production of bromo derivatives of aromatic amines used in industry, technics and technology.

Key words: aromatic amines, anilines, bromination, oxybromination, monobromination, oxidant, halogenation agent, "in situ", regioselectivity, catalyst

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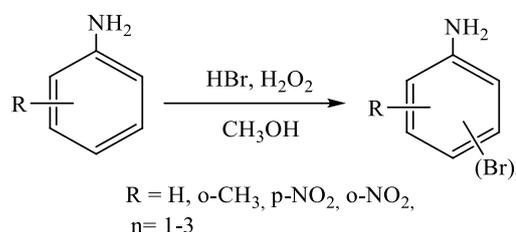
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Taking into account that the brominated derivatives of aromatic compounds are widely used and therefore increased demand for these substances, a number of new methods have developed and reported in the literature. These methods differ from the point of view of the used brominating and oxidizing agent, the medium and the solvent, the catalyst, the effect on the environment, the regioselectivity, the number of bromine atoms in the obtained product.

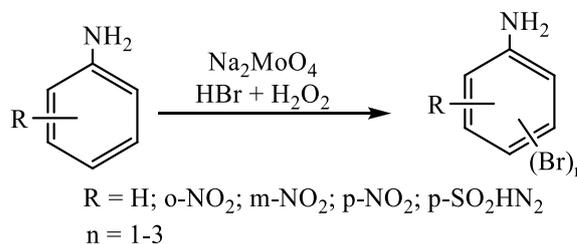
There is information in the literature about the bromination of aromatic amines with different halogenation agents as HBr, KBr, NaBr, NH₄Br, CuBr₂, N-bromosuccinimide, N-bromosaccharin and polymer-supported compounds.

The bromination of aromatic amines with a solution of hydrogen bromide and hydrogen peroxide [1, 2] have been carried out without presence of a catalyst (scheme 1) [3] and in the presence of the sodium molybdate catalyst (scheme 2) [4]. The bromine has been formed "in situ" and from the bromination of various substituted anilines the mono-, di-, tribromo- substituted derivatives have been obtained. It was investigated the influence of the reaction time on the course of the reaction. Thus, the oxybromination reactions of 2-nitroaniline (4-nitroaniline) for 15 min and 20 min been carried out and 4-bromo-2-nitroaniline with 94% yield and 2,4-dibromo-6-nitroaniline 97% yield (2-

bromo-4-nitroaniline with 90% yield and 2,6-bromo-4-nitroaniline with 94% yield) been respectively obtained.



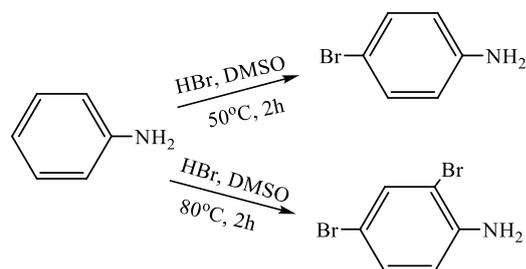
Scheme 1
Схема 1



Scheme 2
Схема 2

Temperature control in the bromination of anilines with the DMSO/HBr system helped to prepare selectively the mono- or dibrominated products (scheme 3) [5]. The use of *trans*-3,5-dihydroperoxy-3,5-dimethyl-

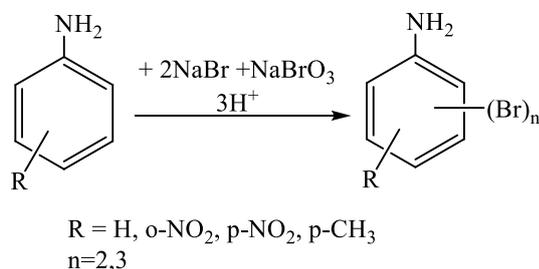
1,2-dioxolane as a new oxidant in bromination of anilines with HBr have been carried out at room temperature in water [6].



Scheme 3
Схема 3

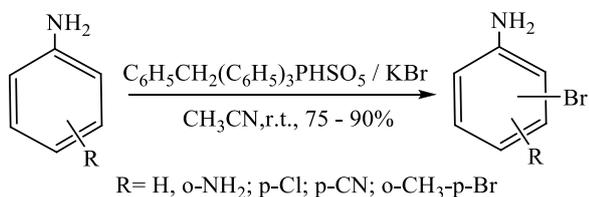
The efficiency of the bromide:bromate reagent at 2:1 ratio has been investigated [7] in bromination of aniline and its derivatives (scheme 4). A molar excess of acid formed a salt with an amine group, after competition of the reaction this mixture was neutralized with sodium bicarbonate. In the bromination of aniline CH₃OH was used as the solvent, but in the bromination of the aniline derivatives CH₂Cl₂ was used as the solvent.

In many cases through the regioselective oxidative bromination of aromatic amines with potassium bromide and benzyltriphenylphosphonium peroxymonosulfate in a neutral reaction condition [8] the monobrominated derivatives (scheme 5) have been obtained.



R = H, o-NO₂, p-NO₂, p-CH₃
n=2,3

Scheme 4
Схема 4



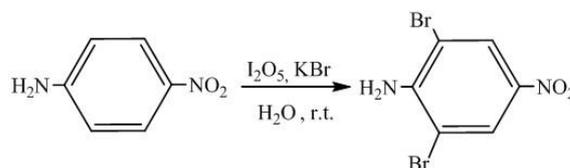
R = H, o-NH₂; p-Cl; p-CN; o-CH₃-p-Br

Scheme 5
Схема 5

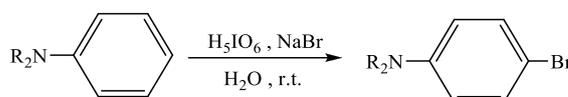
For anilines brominated in anhydrous solution with the use of potassium bromide in the presence of poly(4-vinylpyridine)-supported bromate [9] a high selectivity at the *ortho*- and *para*-positions has been observed.

Hou J. et al. have reported [10] about an ecologically safe method of bromination of 4-nitroaniline

(scheme 6) at room temperature, by use of the I₂O₅-KBr water system. The bromination of aromatic amines in CH₂Cl₂/H₂O with HJO₃/KBr [11] and in water with *ortho*-periodic acid / sodium bromide (1: 2) (scheme 7) [12] has been carried out at room temperature for a short time.



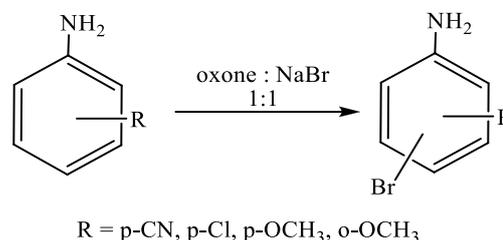
Scheme 6
Схема 6



R = CH₃, C₂H₅

Scheme 7
Схема 7

The bromination of various substituted anilines with oxone and sodium bromide (scheme 8) has been carried out [13] while stirring at room temperature, solutions of anilines, oxone and sodium bromide in 1:1 mixture of CH₃CN/H₂O.



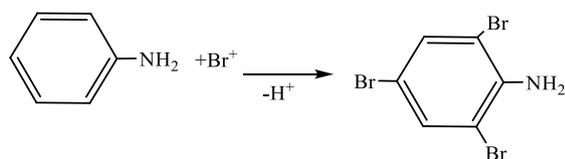
R = p-CN, p-Cl, p-OCH₃, o-OCH₃

Scheme 8
Схема 8

The use of ammonium molybdate as a catalyst in a selective monobromination of various deactive anilines (scheme 9) with potassium bromide and sodium perborate [14] accelerated the reaction, but did not affect on production of a good yield and high selectivity. While without the presence of the catalyst, the reaction has been completed within 14 h, in the presence of the catalyst the reaction has been completed within 2-3 h. With the *ortho*-halogenated anilines it has been achieved the excellent results, bromination of *ortho*-nitroaniline gives a mixture of mono- and polybrominated compounds.

“Sono-halogenation” of aromatic amines with potassium bromide has been carried out under ultrasound in two-phase carbon tetrachloride/water (CCl₄/H₂O) conditions [15] and nuclear bromination with an electrochemical method has been carried out by two-phase

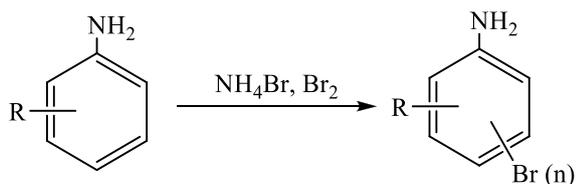
electrolysis (scheme 10) [16]. An electrolyte bromine source (solution of 5% HBr with 50-60% NaBr) was used as an upper phase. The substrate dissolved in chloroform was used as a low phase. This electrochemical method gave a high yield (70-98%) of monobrominated compounds and a high regioselectivity at *para*-position (>95%).



Scheme 10
Схема 10

Halder J. has reported [17] "*in situ*" formation of bromine by using sodium bromide and 1(M) HCl household bleach and about bromination of active aromatic compounds with the reaction of aromatic electrophilic substitution. The bromination of aniline at 0 °C for 2 h have resulted with a 75% yield at 80:20 ratio of *ortho:para* bromoaniline.

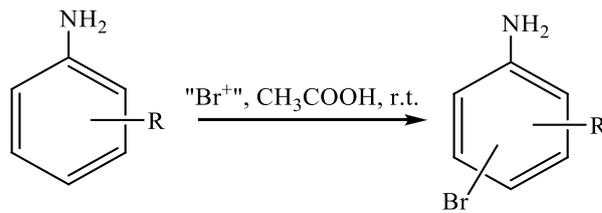
In oxybromination of aromatic amines with NH₄Br–Br₂ system (scheme 11), NH₄Br was used as a source of bromine and Br₂ as an oxidant [18]. The number of bromine atoms in the product depended on the reaction time: from the 2-nitroaniline 4-bromo-2-nitroaniline (15 min) and 2,4-dibromo-6-nitroaniline (20 min); from the 4-nitroaniline 2-bromo-4-nitroaniline (15 min) and 2,6-dibromo-4-nitroaniline (20 min) were obtained.



R = H; o-NO₂; m-NO₂; p-NO₂; p-SO₂NH₂
n = 1-3

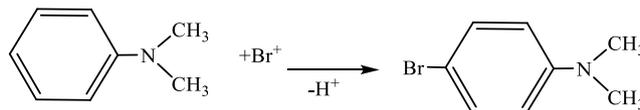
Scheme 11
Схема 11

By use of oxone as an oxidizer in oxybromination of aromatic amines with the ammonium bromide [19] within a short period the monobrominated compounds in high yield have been obtained (scheme 12). In oxybromination of anilines (scheme 13) with NH₄Br/H₂O₂ system without a catalyst in acetic acid, the electrophilic substitution of bromine has been formed "*in situ*" [20].

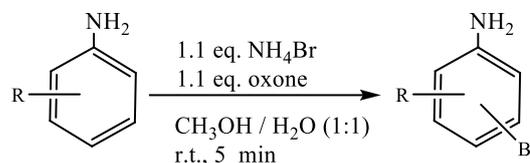


R = o-Br, o-I, o-F, o-NO₂, p-Br, p-I, p-F, p-NO₂

Scheme 9
Схема 9

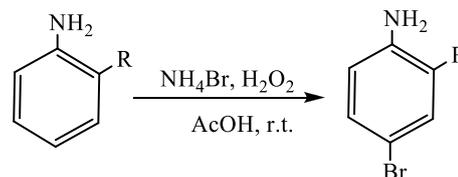


Scheme 10
Схема 10



R = CN, CH₃O₂C

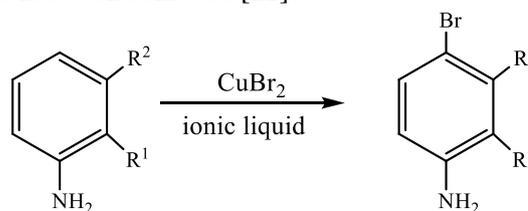
Scheme 12
Схема 12



R = H, CH₃, Cl, CN, NO₂, COOH

Scheme 13
Схема 13

The copper (II) bromide was an effective reagent for monobromination [21] of aromatic amines at room temperature, the reaction proceeded with selectivity and with production of the corresponding monobrominated compounds. Using of ionic liquids as a solvent in bromination of unprotected anilines at *para*-position with copper (II) bromide (scheme 14) the high yield has been achieved [22].

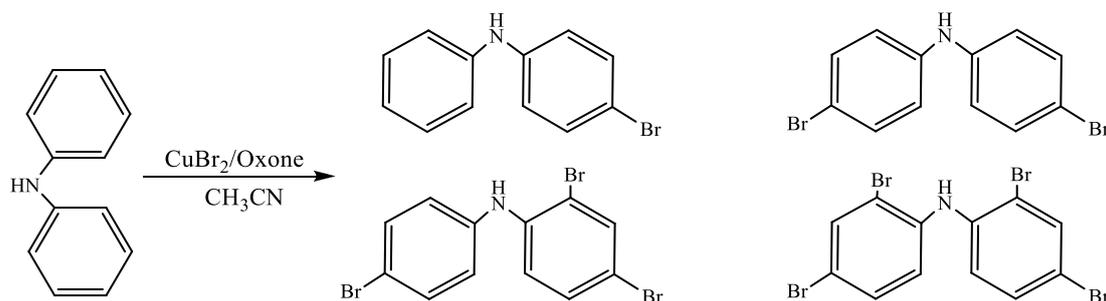


R¹ = CH₃, OCH₃, F, CF₃, NO₂; R² = H
R¹ = H; R² = CH₃, OCH₃, F, CF₃

Scheme 14
Схема 14

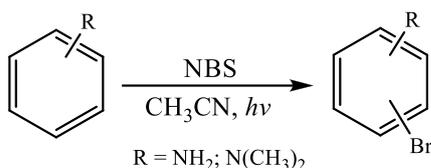
The compatibility of the copper bromide (II) with oxone is presented as a simple and effective reagents for the bromination of aromatic amines (scheme 15),

and primary, secondary, tertiary aromatic amines as the appropriate substrates [23]. Mono- and multi-brominated products have been obtained.



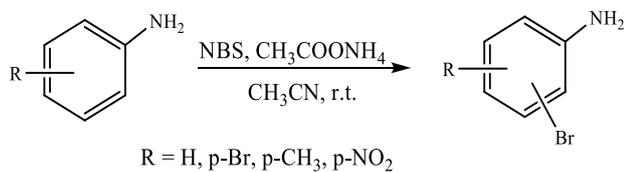
Scheme 15
Схема 15

In regioselective atomic bromination of aromatic compounds by using of brominating agent N-bromosuccinimide (NBS) with ultraviolet radiation (scheme 16) it has been observed the preparation of mono-bromine compounds [24]. The reaction has been carried out at room temperature (30 ± 2 °C) without use of any catalyst. The selectivity of bromination depended on the nature of the substituent on the aromatic ring.

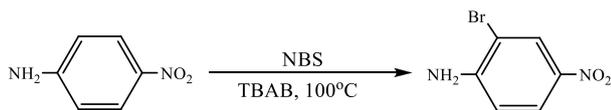


Scheme 16
Схема 16

By using of NBS it has been carried out the *para*-selective monobromination of anilines in the presence of ammonium acetate as a catalyst at room temperature (scheme 17) [25] and in tetrabutylammonium bromide (TBAB) (scheme 18) [26].



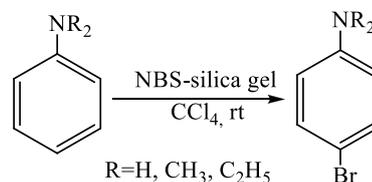
Scheme 17
Схема 17



Scheme 18
Схема 18

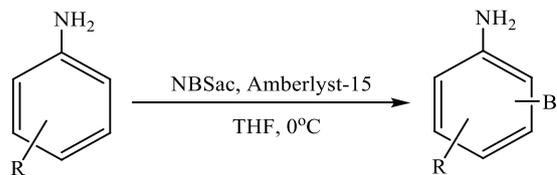
Through nuclear bromination of some substituted anilines in the solid state with NBS the experimental and theoretical investigations have been carried

out [27]. In a solid state, the reactivity depended on the reaction time, on the temperature and on the nature of substrate substituents. During carrying out of the reactions in the alloy or in solution with a decrease in the selectivity, the yield of the product has been decreased. The experiments carried out by using NBS in bromination of aromatic amines (scheme 19) at room temperature in carbon tetrachloride with catalytic action of silica gel have been resulted by the production of *para*-bromo derivatives and *ortho*-bromo derivatives in a case of *para*- position substituent [28].



Scheme 19
Схема 19

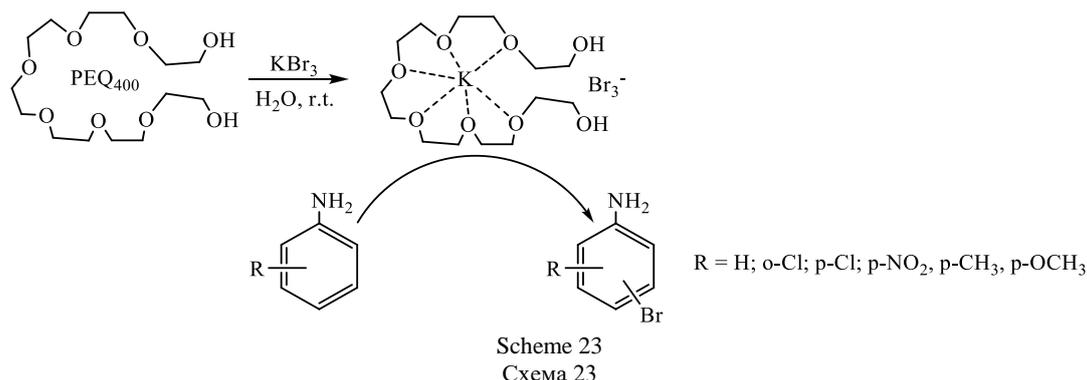
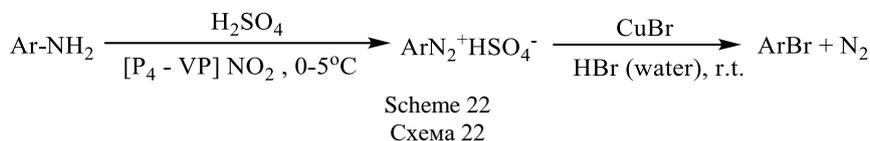
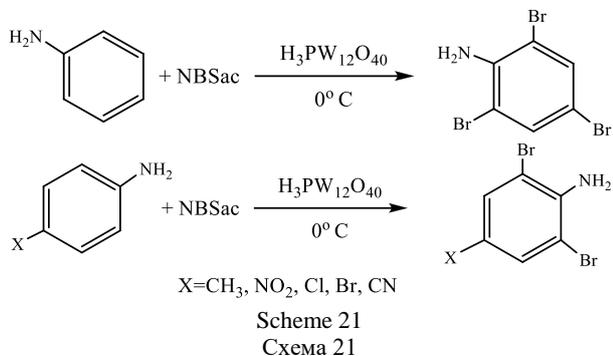
It has been reported about bromination of aromatic amines by using N-bromosaccharin (NBSac) in the catalytic amount of Amberlyst-15 (scheme 20) [29] and directed bromination of anilines with NBSac, by use of tungstophosphoric acid as a heterogeneous recyclable catalyst, under solvent-free conditions [30, 31].



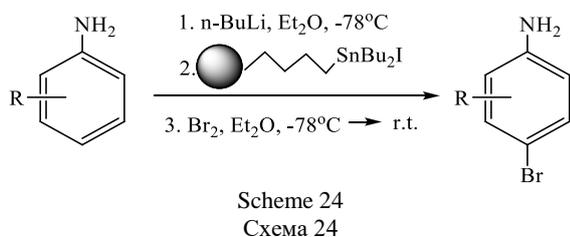
Scheme 20
Схема 20

The aniline and some of its derivatives have been brominated (scheme 21) by use of NBSac and in

the presence of $H_3PW_{12}O_{40}$ catalyst. For show the application and generality of this method the authors have brominated the anilines and phenols. On the basis of the obtained results, it was determined that the functional groups on the aromatic ring did not affect the reactivity.



In regioselective bromination of aromatic amines there have been used the polymer-supported organotin reagents (scheme 24) [36], and N,N,N',N'-tetrabromobenzene-1,3-disulfonylamide (TBBDA) and poly (N-bromobenzene-1,3-disulfonylamide) (PBBS) (scheme 25) [37].

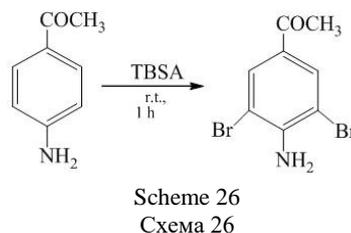
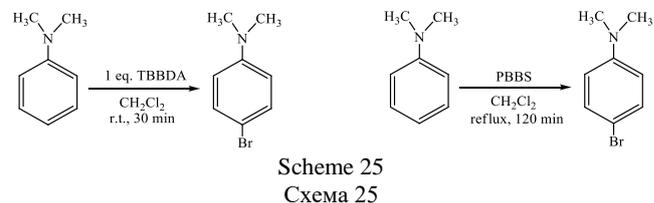


Since the tribromoisocyanic acid (TBSA) is the source of three halogen atoms it is presented as a good reagent for the direct solvent-free bromination of

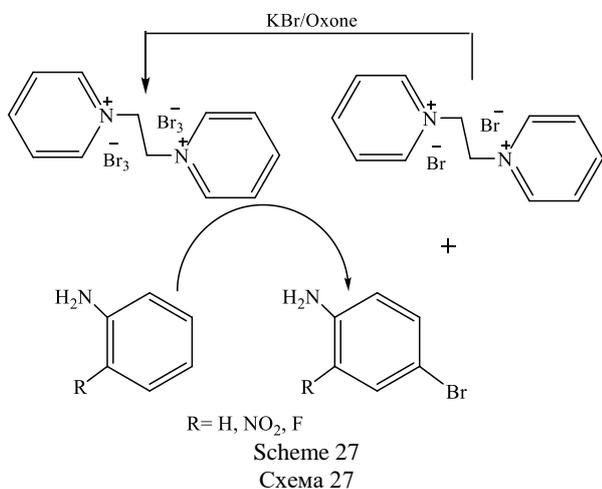
Zarchi M.A.K. et al. have reported [32, 33] about diazotization-bromination of arylamines by using of poly (4-vinylpyridine)-supported ethyl bromide and cross-linked poly(4-vinylpyridine) -supported nitrite ion ($[P_4-VP]NO_2$) (scheme 22).

The synthesized complex from the complexation of KBr_3 with acyclic poly(ethylene glycol) was shown as a regioselective, selective and effective reagent for monobromination of aromatic amines in the mild reaction condition (scheme 23) [34]. Through the bromination of N,N-alkylated amines at ambient temperature with a polyvinylpyrrolidone-bromine complex the monobrominated products with good yield have been obtained [35].

electron rich aromatic compounds [38]. Through the bromination of 1-(4-aminophenyl)ethanone 1-(4-amino-3,5-dibromophenyl)ethanone with 95% yield has been obtained (scheme 26).



1,2-Dipyridine ditribromide-ethane was synthesized and investigated as brominating agent in bromination of some aromatic amines (scheme 27). At any stage of reaction no solvent was used and the solid product was obtained [39].

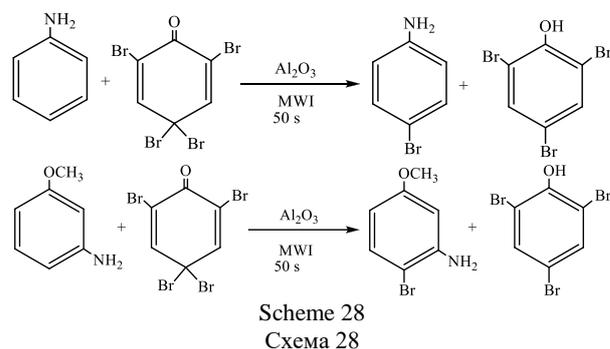


By use of quaternary ammonium tribromide the method of aromatic bromination without a solvent has been developed. In this work [40] it has been reported about some bromination reactions in the thermal and microwave medium without the use of any solvent. In the bromination of the organic substances the various reagents of quaternary ammonium tribromides – tetrabutylammonium tribromide, tetraethylammonium tribromide, cetyltrimethylammonium tribromide, tetramethylammonium tribromide have been used and with the aim of determination of the universality of these reagents without solvent the various classes of organic substances have been chosen. The reaction of activated aromatic compounds with these reagents in the thermal and microwave conditions has been resulted in preparation of *para*-bromine products. The bromination of aniline due to the effect of the cationic part of the tribromide reagent has been resulted in preparation of *para*-bromine products and *ortho*-substituted side products.

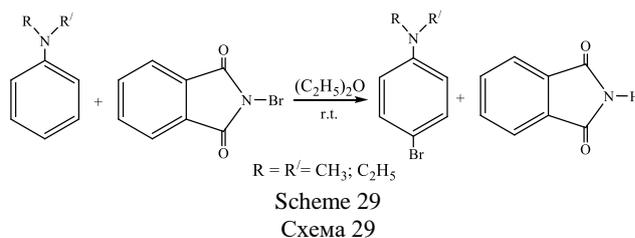
In contrast to the standard methods of bromination through the encapsulated in β -cyclodextrin aniline and N-methylaniline there have been obtained the *ortho*-bromanilines and *para*-bromo-N-methylanilines in good yield [41]. It has been reported about the ecologically pure method of bromination of anilines with gaseous bromine and brominated reagent in the solid state [42]. In most cases, the reactions carried out in a solvent-free medium showed a higher yield and selectivity than the reactions occurring in the solvent.

2,4,4,6-Tetrabromocyclohexa-2,5-dienone in dichloromethane or chloro-form has been used as the

halogenation reagent for bromination of aromatic amines, the monobrominated products with superiority at *para*- position or only at *para*- position have been obtained [43]. The protection of the amine group was not required, a yield is higher than 90%. The high selectivity for a short reaction time, atomic economy, recyclization of the reagent have been shown as the advantages of bromination of aromatic compounds by using of 2,4,4,6-tetrabromo-2,5-cyclohexadienone in conjunction with microwave and ultraviolet radiation [44]. The nuclear bromination of aromatic amines has been carried out with reactants adsorbed on solid support and exposed to microwave radiation (scheme 28).

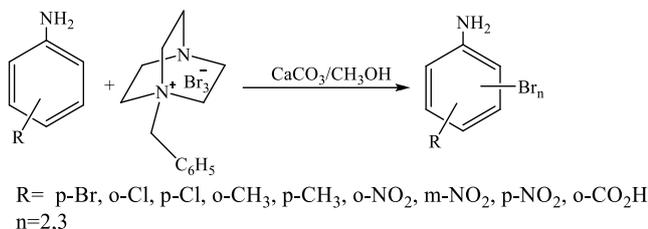


By using N-bromophthalimide the bromination method [45] of active aromatic rings has been developed. From the reactions of N,N-dimethylaniline and N,N-diethylaniline with N-bromophthalimide in diethyl ether at room temperature there have been obtained the *para*-bromo isomers with a good yield (scheme 29).



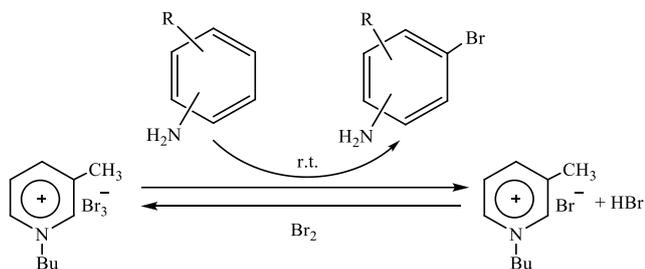
The reaction of anilines, *ortho*- and *meta*-substituted anilines and N,N-dialkyl-anilines in sulfuric acid with bromine and nitrosonium hydrogen sulphate has been resulted in preparation of 4-bromoanilines. The bromination process did not proceed without the presence of the nitrosonium ion [46]. As a result of the reacting anilines and benzyltriphenyl-phosphonium tribromide in condition of dichloromethane and methanol in the presence of sodium bicarbonate at room temperature for several minutes the polybromoanilines were obtained [47].

Through the bromination of anilines with 1-benzyl-4-aza-1-azoniabicyclo [2.2.2]octane tribromide in the presence of a small amount of methanol and CaCO₃ the brominated aromatic amines have been obtained [48]. 1-benzyl-4-aza-1-azoniabicyclo [2.2.2]octane tribromide is shown as an effective reagent for the bromination of aniline derivatives, the active and non-active aromatic amines have been brominated (scheme 30).

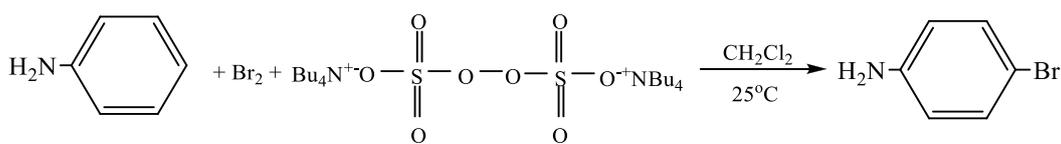


Scheme 30
Схема 30

1-Butyl-3-methylpyridinium tribromide ionic liquid was synthesized and used as a regioselective reagent/solvent for the nucleophilic bromination of various anilines (scheme 31) at room temperature, in most cases the only solvent for the extract was the water [49].



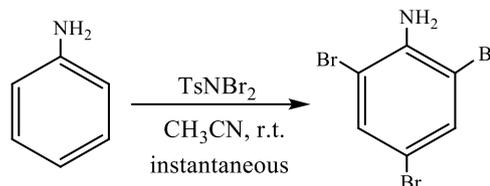
Scheme 31
Схема 31



Scheme 33
Схема 33

Cerichelli G. et al. have reported about the bromination of some N,N-substituted anilines in a homogeneous solvent and in the presence of a suspension of cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium tribromide, cetylpyridinium tribromide, cetylquinuclidium tribromide, cetyltributylammonium tribromide, cetyldimethyl-2-hydroxyethylammonium tribromide, 1,2-bis(cetyl-N,N-dimethylammonium)ethane tribromide, 1-hexadecylpyridinium tribromide surfactants in water [54-57]. In contrast to the homogeneous

N,N-Dibromo-p-toluenesulfonamide (TsNBr₂) was shown [50] as a new brominating reagent for the bromination of aromatic compounds, the reaction was rapid and with application of this method to various aniline (scheme 32), phenol, anisoles at room temperature there have been obtained the polybrominated aromatic products.

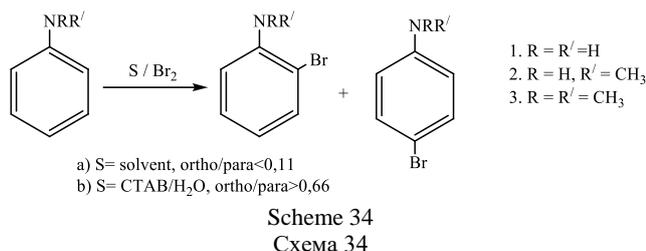


Scheme 32
Схема 32

Kumar L. et al. have reported [51, 52] about the selective bromination of various substituted aromatic compounds of industrial and pharmacological significance with the use of an aqueous solution of CaBr₂-Br₂. The derivatives of anilines and phenols with such strong electron-acceptor groups as carbonyl, nitro showed the good reactivity with the brominating reagent, and in a short reaction time were brominated with good yield (92-98%) and purity (>99%). The resulting by-product (HBr) was effectively used and with renewal of the brominating reagent without loss of selectivity the following bromination was reused. As a result of regioselective direct bromination of the aniline in the presence of the tetrabutylammonium peroxydisulfate (scheme 33) for 1 h with the Br₂ the mono-brominated product with 84 % yields was has been obtained [53].

condition in the presence of surfactants it has been observed an increase of regioselectivity *ortho/para* in the high ratio (scheme 34). In authors' opinion, the regioselectivity depends on nature of the substituents bonded to the nitrogen atom in the aniline and on the temperature.

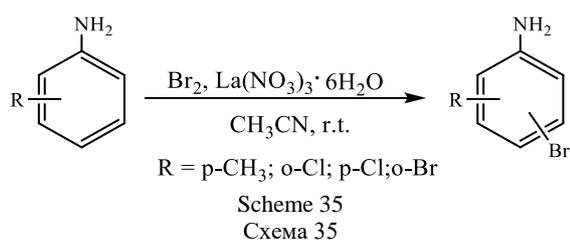
The reaction of the aromatic amines with the benzyltrimethylammonium tribromide in the dichloromethane-methanol (in the composition was a calcium carbonate) for 0.5 h led to the formation of bromine-substituted aromatic amines in good yield [58].



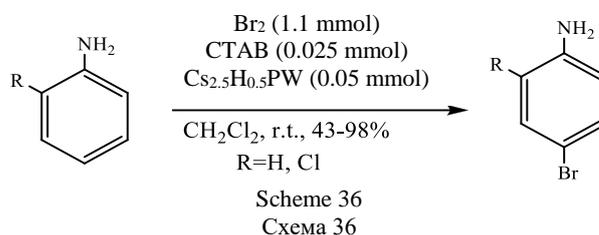
It has been reported about a regioselective method of bromination of the aniline derivatives at room temperature in dichloromethane with ethylenebis(N-methylimidazolium) ditribromide and the possibility of using this isolated reagent several times [59].

By using alkyl bromide and sodium hydride in DMSO, the various aromatic systems with different substituents were brominated [60]. By selecting the corresponding alkyl bromide and controlling its amount a large range of mono-brominated substrates has been obtained. Initially for the bromination of aromatic compounds it has been chosen 2-bromopentane, for increase of the reactivity of the bromination 2-bromopentane was replaced with the ethyl 2-bromopropionate. From the bromination of N,N-dimethylaniline and N,N,3,5-tetramethylaniline with the 2-bromopentane there have been respectively obtained 4-bromo-N,N-dimethylaniline and 4-bromo-N,N,3,5-tetramethylaniline; and from the bromination of N,N-dimethylaniline and N,N-dimethyl-3-nitroaniline with the 2-bromopropionate – 2,4-dibromo-N,N-dimethylaniline and 4-bromo-N,N-dimethyl-3-nitroaniline respectively.

The bromination reaction has been studied with a number of aromatic amines with electron-donor and electron-acceptor substituents at room temperature with La(NO₃)₃·6H₂O catalyst (scheme 35) [61]. It has been observed a higher yield of mono-brominated products in anilines with electron-donor groups than anilines with electron-acceptor groups. The reaction has been carried out in the various proton and aprotic solvents and the acetonitrile (CH₃CN) was the most appropriate for this reaction. The efficiency of La(NO₃)₃·6H₂O catalyst has been investigated by the aniline reaction with elemental bromine, without and in the presence of the catalyst.

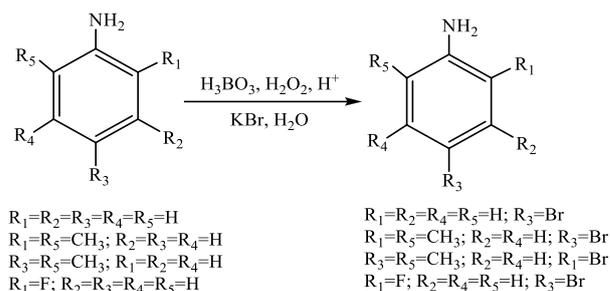


The regioselective bromination of anilines in the presence of the heterogeneous catalytic system Cs_{2.5}H_{0.5}PW₁₂O₄₀/cetyltrimethylammonium bromide gave an effective result (scheme 36) [62].



Environmentally friendly catalytic monobromination of anilines by use of sodium bromide, hydrogen peroxide (35%), cerium (III) chloride as a catalyst, at room temperature or under reflux conditions in water was the regioselective at *para*-position [63]. The regioselective oxybromination of anilines with the ammonium molybdate catalyst [64] was possible with the electrophilic substitution of bromine obtained "in situ" by use of H₂O₂ as an oxidant and KBr as a brominating reagent.

The regioselective bromination of aromatic amines has been carried out (scheme 37) by using of boric acid as a catalyst (reusable), KBr as a source of bromine and H₂O₂ as an oxidant agent [65]. The peroxoborate obtained from the reaction of boric acid with H₂O₂ is shown as the effective catalyst in the selective bromination of organic compounds at room temperature. The high selectivity, mild reaction conditions, the use of H₂O or C₂H₅OH as a solvent have been noted as advantages of this synthetic method.

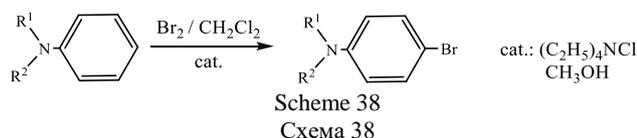


Scheme 37
Схема 37

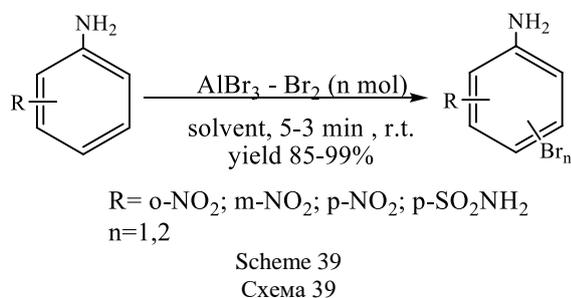
The bromination of the anilines (scheme 38) with high selectivity at *para*- position has been carried out under mild conditions by use of tetraethylammonium chloride/methanol system as a cocatalyst [66].

By use of sodium perborate as an oxidant [67] the oxybromination of aromatic amines has been investigated. The sodium perborate with glacial acetic acid-acetic anhydride, potassium bromide and sodium

volphramate as the catalyst has been shown as a new system for the bromination of aromatic amines. Some reactions have been carried out at room temperature, but the most efficient procedures have been undergone with the heating of the solution at 75 °C. The most reactions were the regioselective, when *ortho*- and *para*-substitution is possible, in both cases the *para*-substituted product was only separated isomer.



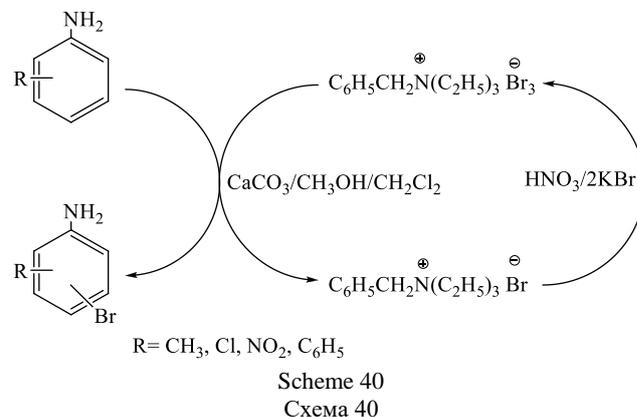
Sharma S.K. has reported [68] about ecologically safe, regioselectivity of the use of $\text{AlBr}_3\text{-Br}_2$ system for bromination of aromatic amines (scheme 39).



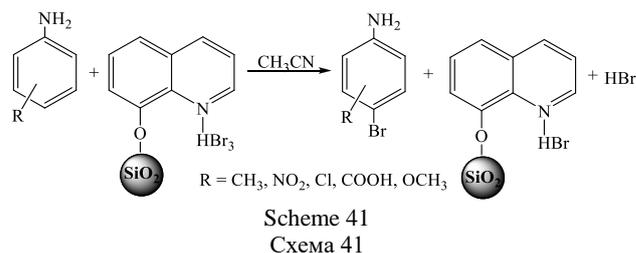
The bromination of economically significant aromatic compounds with $\text{AlBr}_3\text{-Br}_2$ aqueous system without use of the catalyst and oxidant has been carried out. The substituted anilines, phenols, aldehydes and anilides were brominated. The $\text{AlBr}_3\text{-Br}_2$ aqueous system has been obtained by addition of molecular bromine Br_2 to an aqueous solution of aluminum tribromide at room temperature (25±10 °C). The regioselectivity of the reaction depended on the substituent functional groups. The presence of electron-acceptor groups in the aromatic ring significantly reduced the bromination rate of the rings. Depending on the ratio of the starting materials, the various compounds have been obtained. At 1:1:1 ratio of 4-nitroaniline: $\text{AlBr}_3\text{:Br}_2$ 2-bromo-4-nitroaniline, at a 1:2:2 ratio 2,6-dibromo-4-nitroaniline; at 1: 1: 1 ratio of 2-nitroaniline: $\text{AlBr}_3\text{:Br}_2$ 4-bromo-2-nitroaniline and at 1: 2: 2 ratio 2,4-dibromo-6-nitroaniline have been obtained.

The benzyl triethyl ammonium tribromide (BTATE) has been shown as a regioselective brominating agent for aromatic compounds in the presence of a mixture of methanol/dichloromethane solvent, calcium carbonate at room temperature [69]. Among the compounds used in this method there are also anilines (scheme 40), some of which have been immediately converted into new compounds. Most of the reactions

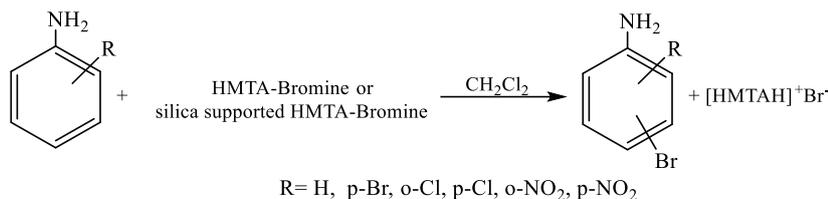
were the regioselective, when *ortho*- and *para*-substitution is possible, in both cases the *para*-substituted product was only isolated isomer. *para*-Substituted aromatic compounds have been brominated at the *ortho*-position. In the presence of electron-acceptor groups in the aromatic ring, the bromination rate decreased, and the presence of electron-donor groups increased.



The silica-supported quinolinium tribromide (SXTB) has been synthesized and used in regioselective bromination of aromatic amines (scheme 41) as an effective solid brominating reagent [70]. It has been investigated the effect of a solvent on the bromination reaction with SXTB. In CH_2Cl_2 , $\text{C}_2\text{H}_5\text{OH}$, DMF, 1,4-dioxane, DMSO and CS_2 the reaction did not occur, in CH_3CN the products with high selectivity have been obtained. The compounds with electron-donor groups are brominated faster than compounds with electron-acceptor groups. In the presence of substituents at *para*-position of the anilines, the substituent reaction proceeded at *ortho*-position with mono-bromine selectivity.



It has been reported [71] about a regioselective method for the bromination of aromatic compounds in dichloromethane with hexamethylenetetramine-bromine (HMTAB). The selectivity depends on the temperature and on the nature of the substituent. When the substituent in the aniline molecule in the 2-position the bromine atom enters the 4-position, in the 4-position – the 2-position (scheme 42).



Scheme 42
Схема 42

Taking into account that the anti-pyrenes, biological active substances, pharmacological preparations on the basis of bromine-containing aromatic compounds are widely used in the industry, the investigations carried out in the field of preparation of such are of great importance.

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