

SYNTHETIC POTENTIAL OF 9,10-ANTHRAQUINONYLDIAZONIUM SALTS

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For the first time, the literature sources concerning the chemical transformations of diazonium salts of 1(2)-amino-9,10-anthracenediones are generalized and systematized. The potential of 9,10-dioxoanthracenyldiazonium salts as key substrates in the preparation of various linear-functionalized, acyclic and heterocyclic derivatives has been determined. The main synthetic transformations of diazonium salts of amino-9,10-anthracenediones, which are realized without preserving the azo function lead to the formation of reaction products of Sandmeyer, Meerwein, and Gomberg–Bachmann–Hay, are analyzed. The use of 9,10-dioxoanthracenyldiazonium salts or products of their transformations for obtaining heteryl-containing condensed and functionalized derivatives is presented.

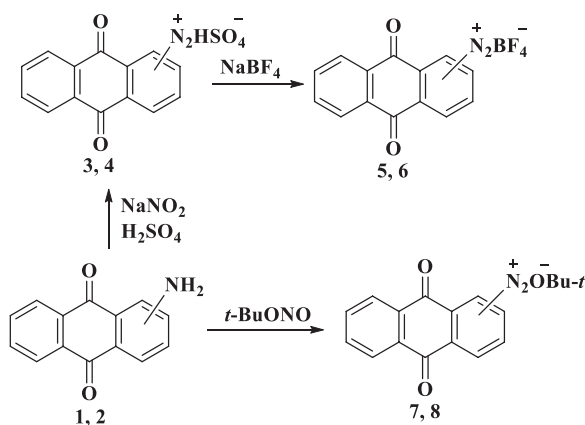
Key words: diazonium salts of 1(2)-amino-9,10-anthracenedione, dediazonation, azo coupling, annulation, heterylfunctionalization.

INTRODUCTION. In modern organic synthesis diazonium salts belong to the important classes of compounds with a powerful synthetic potential, which have not lost their relevance and importance to this day due to their easy accessibility and pronounced reactivity. Their use in various synthetic transformations opens access to new types of organic compounds. In this context, diazonium salts of amino-9,10-anthracenediones play an important role in developing approaches to the synthesis of new substances with potential biological effects. At the same time, despite the diversity of the products of the arendiazonation reaction, a relatively little arsenal of derivatives

was obtained on the basis of diazonium salts of amino-9,10-anthracenediones, among which diazo compounds and the products of the Sandmeyer and Meerwein reactions should be noted.

The formation of 9,10-anthracenediazonium salts occurs only in solutions of concentrated acids, which is due to the decreased basicity of the amino group of amino-9,10-anthracenediones [1]. Usually, 9,10-dioxoanthracenyldiazonium chloride is obtained in the presence of concentrated HCl in organic solvents [1, 2]. However, most often in diazotization reactions, hydrosulfate and tetrafluoroborate salts 3–8 are obtained, which are more

stable during storage and convenient in use. Diazonium hydrosulfates **3**, **4** are easily formed in concentrated H_2SO_4 under the action of sodium nitrite or nitrosyl sulfuric acid [3]. When the latter interact with sodium tetrafluoroborate, they give the corresponding salts **5** and **6** [1]. In recent years, *t*-BuONO is used as an effective diazotizing agent, which makes it possible to obtain salts **7**, **8**.



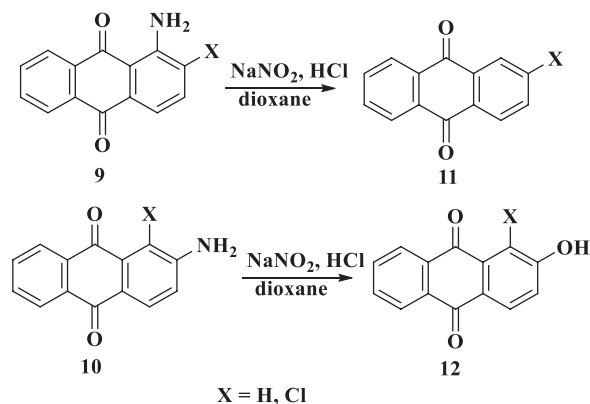
Due to the high electrophilicity of the diazonium center, which is enhanced by quinoid conjugation, salts **3**–**8** easily interact with nucleophilic reagents, which allows the introduction of new substituents into the anthracenedione ring and to obtain both dediazonation products and azo group derivatives.

This review focuses on the generalization and systematization of the results of original studies related to the transformation of diazonium salts of amino-9,10-anthracenediones, and the uses of diazotation reaction products to obtain various derivatives of 9,10-anthracenedione are presented.

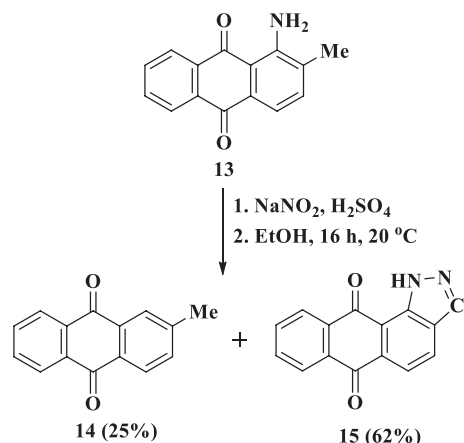
REACTIONS OF DEDIAZONIZATION OF 9,10-ANTHRACENYL DIAZONIUM SALTS

The authors of [3] found that the diazotization of 1(2)-aminoanthracene-9,10-diones **9**

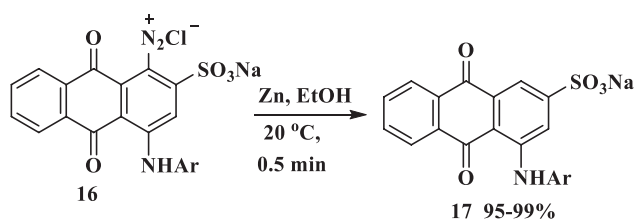
and **10** in dioxane using the NaNO_2 -HCl system leads to the products of the replacement of the diazonium group with hydrogen atom **11** and OH-group **12**. The formation of the latter derivative is explained by the *peri*-effect of diazo and hydroxy groups, which causes the reduction process.



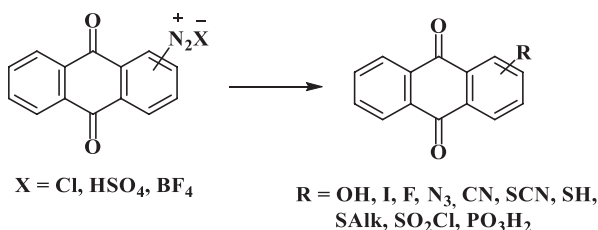
Deaminated methyl derivative **14** and pyrazoloanylelated compound **15** are the products of the conversion of diazonium hydrosulfate of 1-amino-2-methyl-9,10-anthracenedione **13** in methanol and dioxane [4].



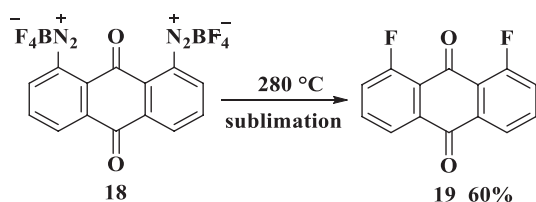
The treatment of 9,10-dioxoanthracenyl-diazonium **16** chlorides with zinc dust in ethanol solution was a convenient approach to the synthesis of reduction products **17** [4].



It should be noted that the introduction of the hydroxyl group, halogen atom, azide, nitrile, sulfur- and phosphorus-containing substituents by replacing the diazonium group of 9,10-anthracenedione is widely used in synthetic practice since the early XX century [1].



Hydroxyderivatives are easily obtained by the hydrolysis of diazonium salts of aminoanthracene-9,10-diones [3, 5, 6]. The interaction of the corresponding diazonium salt with potassium iodide at room temperature is used to obtain 1(2)-iodo-9,10-dioxoanthracene [7]. The one-step interaction of 1(2)-amino-9,10-dioxoanthracene with the diazotizing NaNO₂-HI system in dimethyl sulfoxide medium allows one to obtain the target product with higher yield [8]. The corresponding 1,8-difluoro derivative **19** was obtained under the conditions of the Baltz-Schiman reaction from bis-tetrafluoroborate 9,10-dioxoanthracenyl diazonium **18**.



Nitrile-containing 9,10-dioxoanthracenes are usually obtained under the conditions of the Sandmeyer reaction in the presence of an aqueous solution of a complex salt of copper (I) cyanide and potassium/sodium cyanide [1, 9].

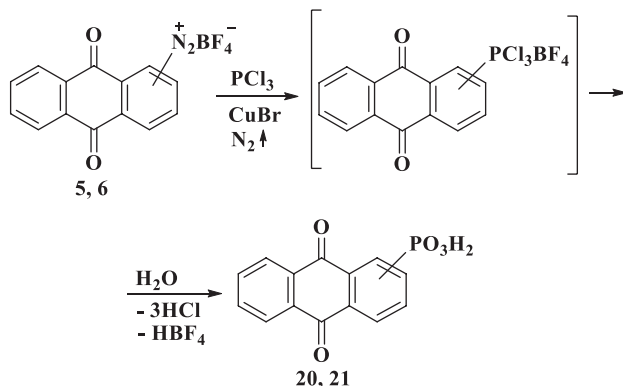
The formation of 1(2)-azido derivatives of 9,10-anthracenedione easily occurs when the corresponding diazonium salts interact with sodium azide in an aqueous medium [10-12].

The synthesis of 1-mercapto-9,10-anthracenedione involves a two-stage process, in which the first stage is carried out by the thiocyanation of the diazonium salt with potassium rhodanide, and the second stage involves alkaline hydrolysis in an aqueous-ethanolic solution [1]. An alternative method of obtaining such a compound is the interaction of 9,10-dioxoanthracenyldiazonium hydrosulfate with potassium dithiocarbonate in an aqueous medium followed by hydrolysis [13].

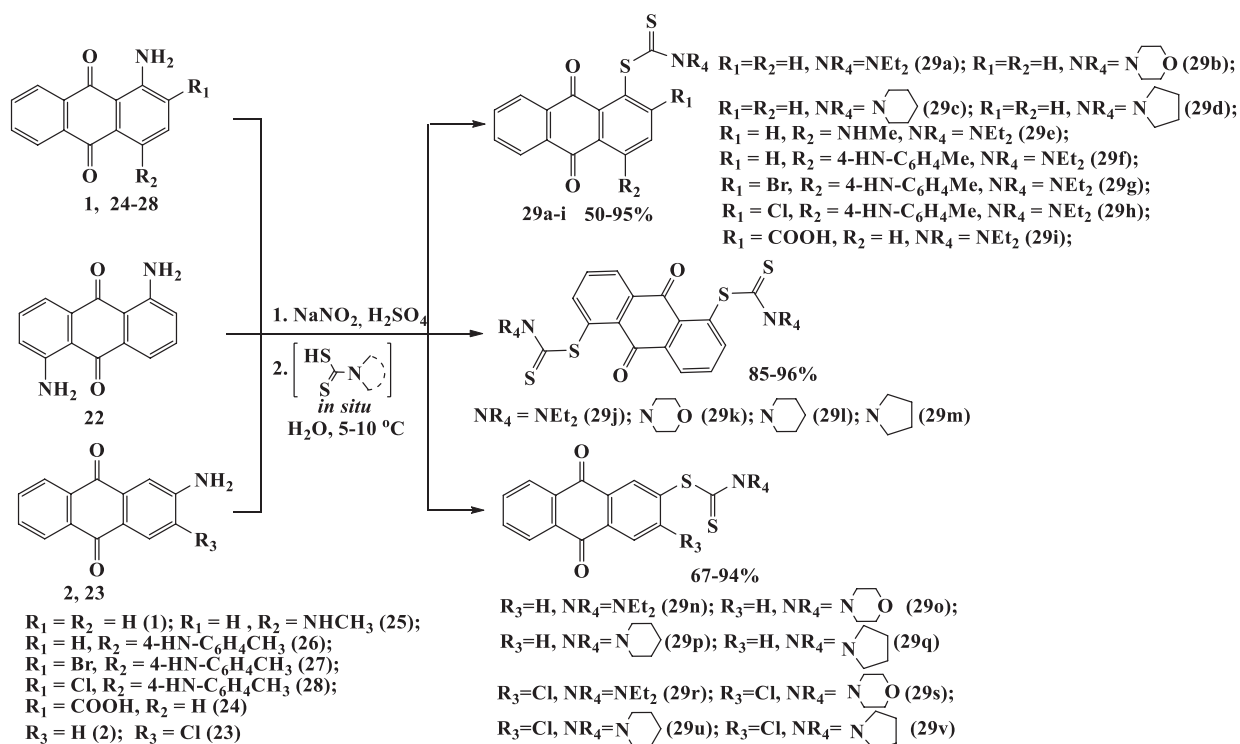
Thiocyanate derivatives were obtained by the diazotization of 1-amino- and 1,4-diamino-9,10-dioxoanthracene with sodium nitrite in sulfuric acid, followed by the action of potassium thiocyanate [14, 15].

Several studies on the synthesis of 1(2)-thio-containing 9,10-anthracenediones by the S-arylation of thioglycolic acid with diazonium salts have been described in the literature [14, 16]. 9,10-Dihydro-9,10-dioxoanthracene-2-ylsulfonyl chloride was obtained from the corresponding diazonium chloride and sulfur (IV) oxide in the presence of copper (II) chloride [17]. Phosphorus-containing derivatives based on diazonium tetrafluoroborates of 9,10-anthracenedione are represented by (9,10-dioxo-9,10-dihydroanthracene-1(2)-yl) phosphonic acids **20**, **21**, which are formed by the interaction of salts **5**, **6** with phosphorus (III) chloride in the presence of a salt of

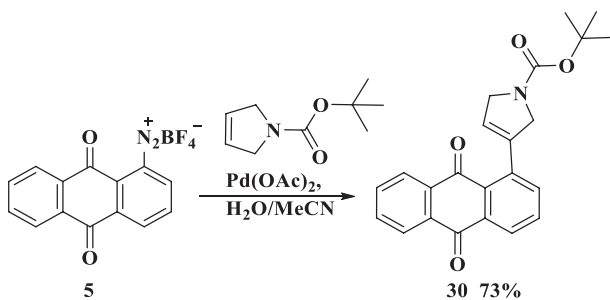
copper (I) and can be easily converted into ammonium salts [18, 19].



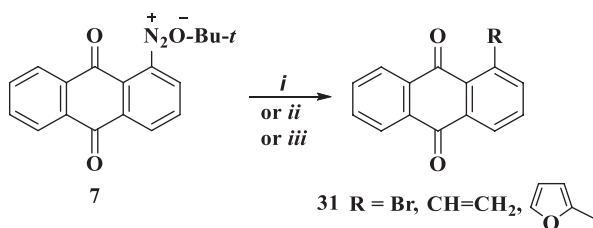
The authors of [20] proposed an effective variant for obtaining 9,10-dioxo-anthracenyldithiocarbamates under the conditions of “green” chemistry based on 9,10-dioxoanthracenyldiazonium salts. The reaction of noncatalytic arylation with freshly obtained, neutralized with sodium carbonate, diazonium hydrosulfate salts of 1(2)-amino-9,10-anthracenediones **1**, **2**, **22–28** and a series of *in situ* generated dithiocarbamic acids with fragments of diethylamine, pyrrolidine, piperidine and morpholine in an aqueous medium under mild temperature conditions led to the preparation of carbodithioates **29a–v**.



9,10-Dioxoanthracenyl-2-diazonium tetrafluoroborate **5** is a convenient reagent in the synthesis of (*N*-Boc-3-pyrrolyl)anthracene-1-yl-9,10-dioxoanthracene **30** under the conditions of Pd-catalyzed arylation of *N*-(*tert*-butoxycarbonyl) -3-pyrroline salt **5** [21].



The authors of [22-28] described the use of diazonium salt **7** to obtain functional derivatives **31** in the presence of copper (II) salts.



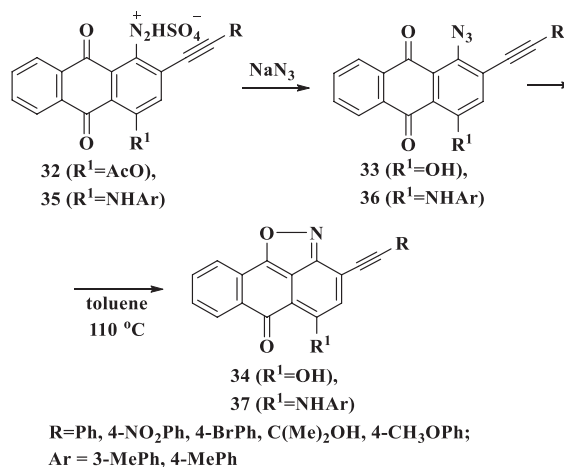
i - CuBr₂, MeCN, 14 h, 20 °C, 70%;

ii - CuBr₂, MeCN, 14 h, 20 °C, TBAF, Pd(dba)₂, 2-(di-*tert*-butylphosphino)biphenyl, THF, 20 °C 8 h, 80 °C, 96%;

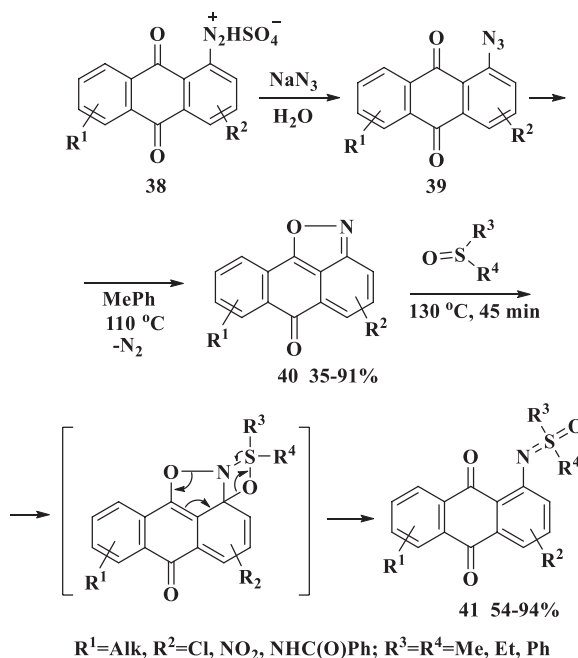
iii -CuBr₂, MeCN, *L*-ascorbic acid, DMSO, 12 h, 20 °C 70%

The influence of electron-donor substituents in the fourth position of the 9,10-dioxoanthracene nucleus on the cyclization process of alkyne-containing hydrosulfate diazonium salts **32**, **35** was determined [29].

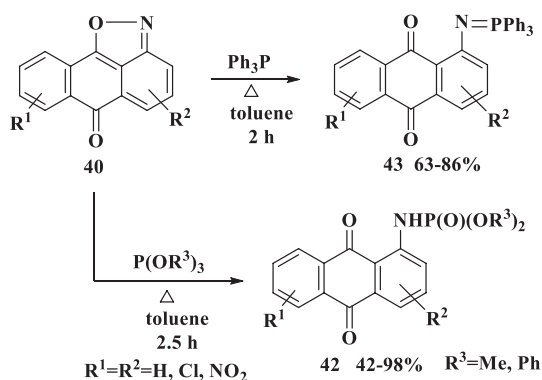
The presence of such substituents not only stabilizes the latter, but also allows the nucleophilic substitution of the diazo group with the azide anion and the conversion of compounds **33**, **36** to isoxazoles **34**, **37** without involving acetylene function.



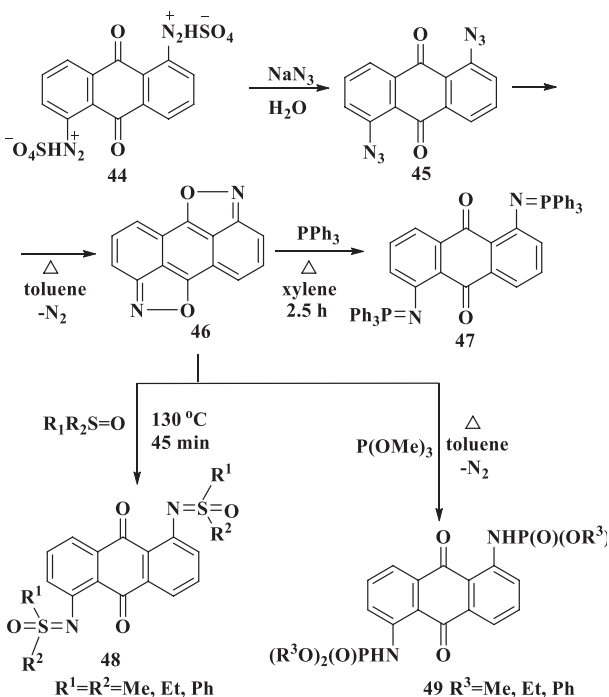
Azidoderivatives **39** under heating above 110° C were converted to compounds of isoxazole type **40**, which reacted with sulfoxide to give sulfanylideneaminoanthracene-9,10-diones **41** [30].



Isoxazole derivatives **40** can also be used to prepare phosphoamides **42** and iminophosphoranes **43** [30].

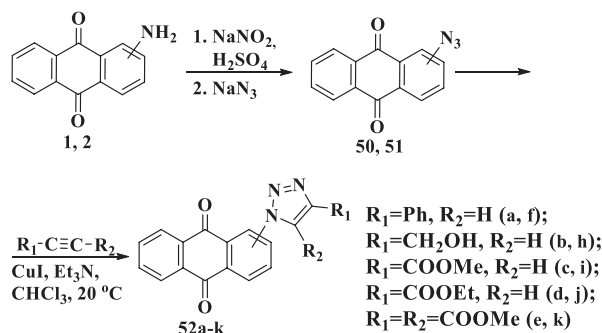


Anthra[1,9-*cd*:5,10-*cd'*]diisoxazole 46 reacts similarly with triphenylphosphine, dimethyl(diethyl, diphenyl)sulfoxides and trialkyl(aryl)oxyphosphines with the disclosure of both isoxazole cycles and the formation of corresponding bisproducts 47–49 [30].



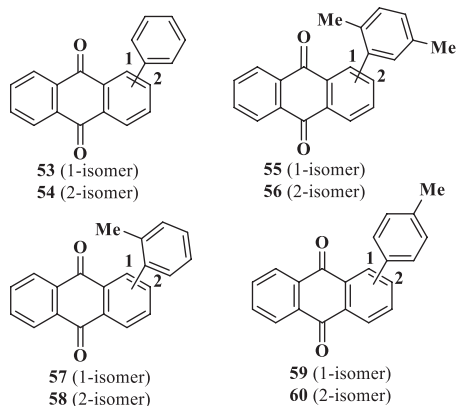
The behavior of the azides of 9,10-anthracenedione 50, 51 in the reaction of Cu-catalyzed 1,3-dipolar cycloaddition (CuAAC)

with a number of substituted alkynes was investigated [31]. It was found that the use of systems such as CuI-*L*-proline in DMSO, CuSO_4 -potassium ascorbate in a mixture of DMF- H_2O and CuI-TEA in chloroform led to a positive result with obtaining 1,2,3-triazole derivatives 52 only in the case of the latter option [31].

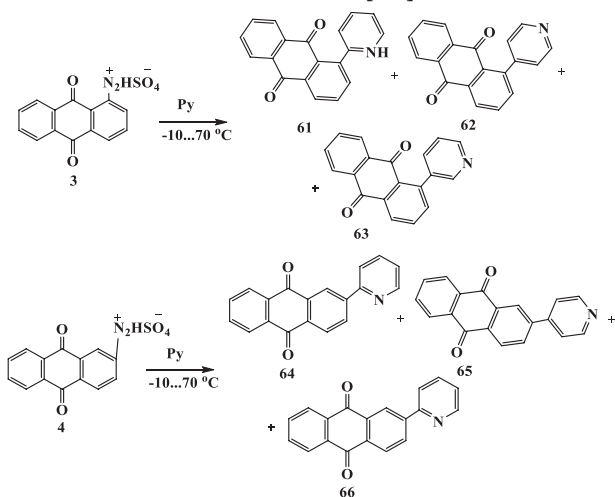


The Gomberg – Bachmann – Hay and Meerwein reactions play an important role in the transformation of the diazonium salts of 9,10-anthracenediones, since the acylation and Friedel – Crafts alkylation processes are not characteristic of 9,10-dioxoanthracene derivatives due to the effect of quinoid conjugation [32].

It was determined that the formation of the products of this reaction, aryl-9,10-dioxoanthracenes 53–60, occurs quite easily and in high yields (40–60%). The arylation of toluene leads to the formation of 1(2)-isomers at the *ortho*- and *para*-positions to CH_3 -groups 57, 59 (in the case of 9,10-dioxoanthracene-1-yl diazonium) and mixtures 58, 60 (in the case of 9,10-dioxoanthracene-2-yl diazonium) [33].

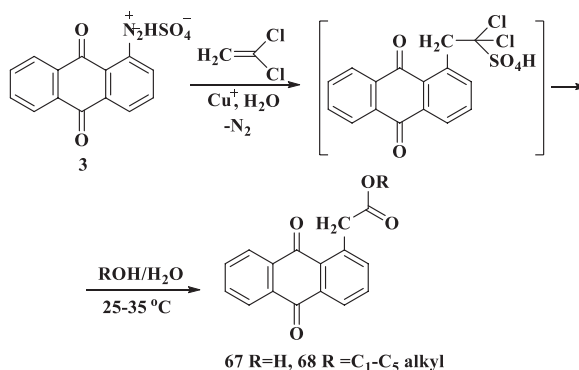


Studies of C-arylation of pyridine by diazonium salts of anthracenediones under the conditions of a modified Gomberg-Bachmann-Hay reaction at a temperature of -10°C to 70°C in the absence of catalyst and Cu-catalysis have shown that a mixture of *ortho*-, *meta*- and *para*-products of arylation of pyridine **61-66** was the result of the interaction [34].

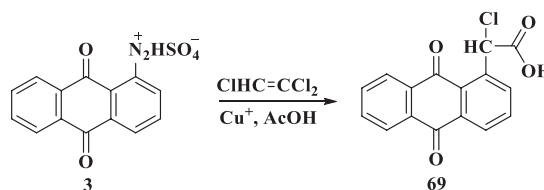


The use of Meyerwein reaction taking diazonium salts of 9,10-dioxoanthracene as an example is represented by coupling reactions with such unsaturated compounds as 1,1-dichloroethene, 1,1,2-trichloroethene, acrylic acid esters, nitrile methacrylic acid, 2,4-dicyano-1-butene in the presence of copper salts [35]. 2-(9,10-Dioxo-9,10-dihydroanthracene-

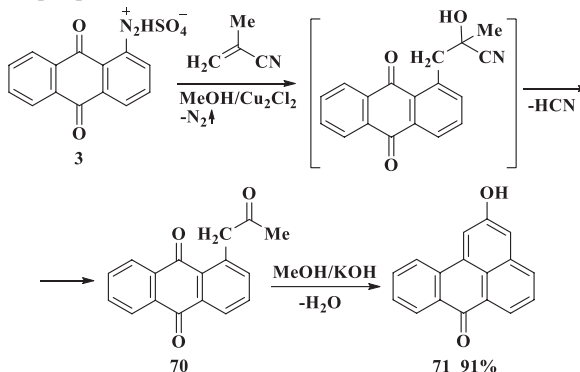
1-yl)acetic acid **67** and its esters **68** were prepared by the Cu-catalyzed coupling of diazonium salt **3** with 1,1-dichloroethene under mild conditions [36].



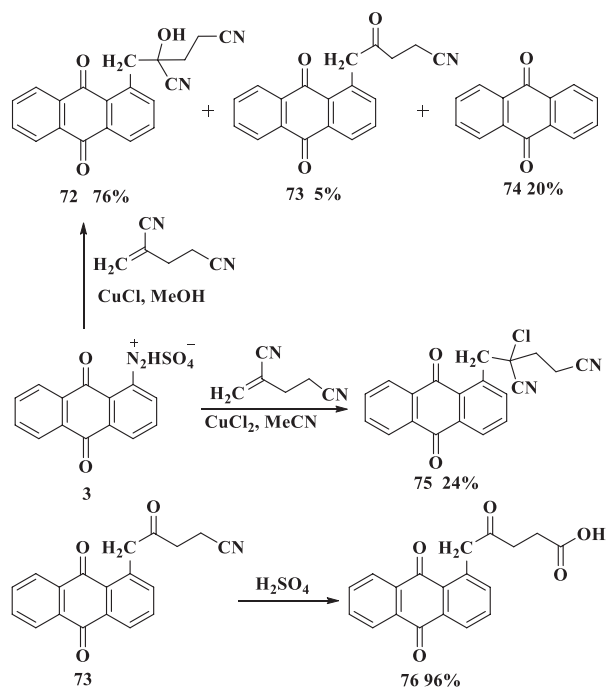
Under similar conditions, 2-(9,10-dioxo-9,10-dihydroanthracene-1-yl)chloroacetic acid **69** was obtained in high yield from 1,1,2-trichloroethene and diazonium hydrogen sulfate **3** in acetate acid [35].



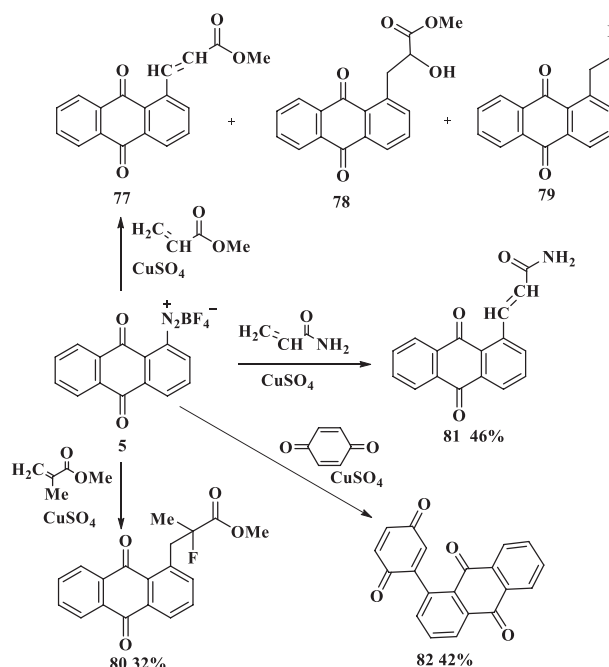
The authors of [35] suggested using methacrylonitrile in the presence of copper(I) chloride to obtain 1-(2-oxopropyl)anthracene-9,10-dione **70**, which was converted by alkaline hydrolysis to 2-hydroxy-7*H*-benzo[*de*]anthracene-7-one **71**.



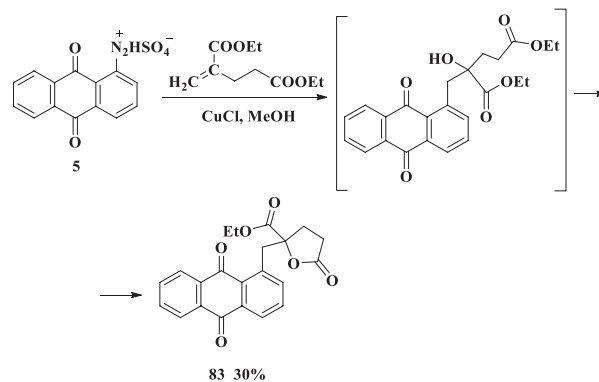
The Cu-catalyzed arylation of 2,4-dicyano-1-butene in methanol leads to the formation of a mixture of cyanohydrin **72**, cyanoketone **73**, and 9,10-dioxoanthracene **74** as a dediazonation product. 5-(9,10-Dioxo-9,10-dihydroanthracene-1-yl)-4-oxopentanoic acid **76** was synthesized by an acid hydrolysis of derivative **73**. When methanol was replaced by acetonitrile, the formation of 2-chloro-2-[(9,10-dioxo-9,10-dihydroanthracene-1-yl)methyl]pentanedinitrile **75** was observed as the main product [35].



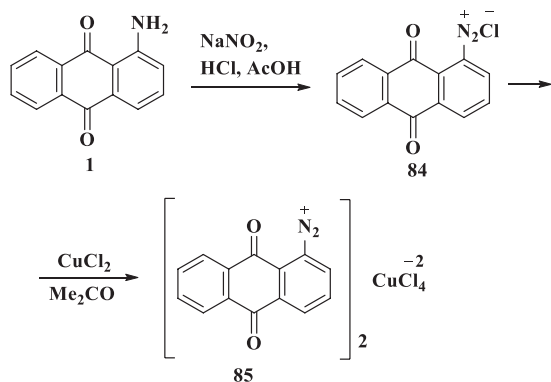
The authors of [2] observed the formation of C-C coupling products **77-82** in the study of the arylation of methyl esters of acrylic and methacrylic acids, acrylamide and 1,4-benzoquinone by 9,10-anthracenedione-1-diazonium tetrafluoroborate under the conditions of Meerwein reaction.



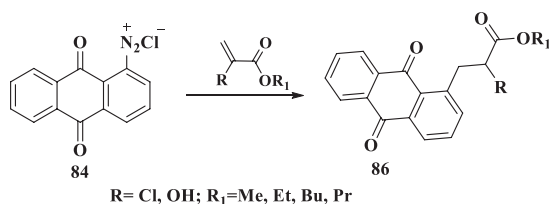
Functionalized with a methylfuran fragment, 9,10-anthracenedione derivative **83** was obtained under the conditions of Meerwein reaction by the arylation of diethyl 2-methyl-ene-pentanedioate in the presence of copper(I) chloride in methanol [35].



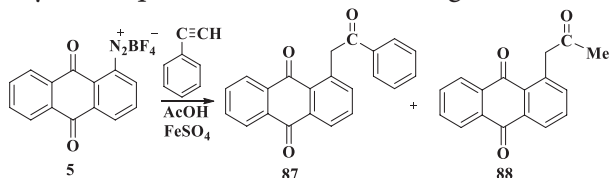
The behavior of 9,10-anthracenedione-1-diazonium chloride **84** was also studied under the conditions of the Meerwein reaction in the presence of CuCl_2 in an acetone medium [37], and it was found that the product of this interaction is tetrachlorocuprate (II) **85**.



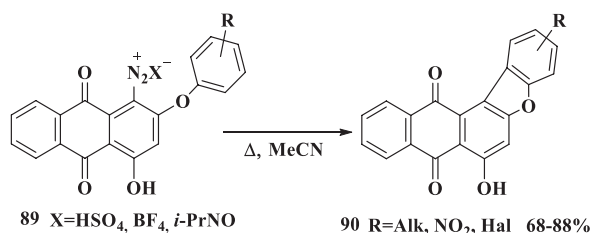
The dediazonation of tetrachlorocuprate (II) **85** in polar solvents at room temperature led to 1-chloro-9,10-anthracenediones. Instead, 9,10-anthracenedione chloro- and hydroxypropionates **86** were obtained in the presence of acrylate esters [37].



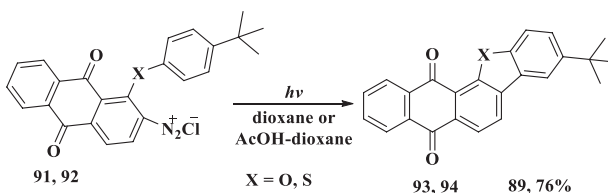
The replacement of CuCl by FeSO₄ leads to the formation of a mixture of ketones **87** and **88**, the yield of which is significantly affected by the sequence of addition of reagents [32].



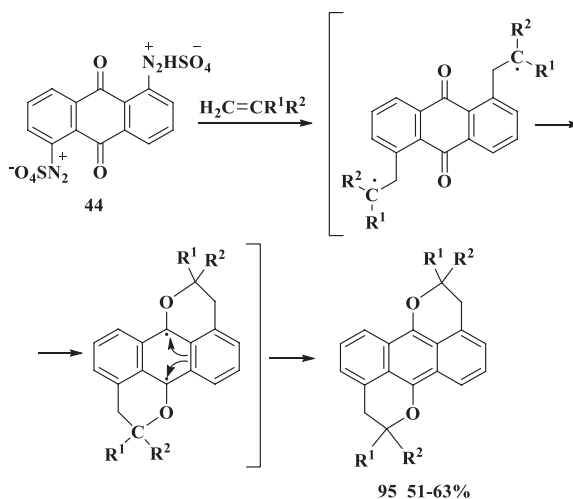
Annulated derivatives of 9,10-dioxoanthracene prepared on the basis of diazonium salts are presented in the literature by a limited number of examples. In particular, a convenient method was proposed for the preparation of benzofuran-dioxoanthracene compounds **90** by heating 4-hydroxy-9,10-dioxo-2-aryloxy-9,10-dihydroanthracene-1-diazonium salts **89** [38].



Moreover, benzofuran- **93** and benzothio-phenene-condensed derivatives **94** of 9,10-anthracenedione were obtained by the photocyclization of 1-aryloxy(aryltio)-9,10-dioxoanthracenyldiazonium chlorides **91** and **92** in dioxane or in a mixture of acetate acid with dioxane [39].



The preparation of condensed tetrahydrodipyranium derivatives **95** was described in [39], where bis(hydrosulfatediazonium)9,10-dioxoanthracene **44** was used in coupling reactions with unsaturated compounds (nitriles of acrylic and methacrylic acids, methyl and ethyl esters of acrylic acid, styrene and methylstyrene) in the presence of copper(I) salts in a dimethylphosphite medium.

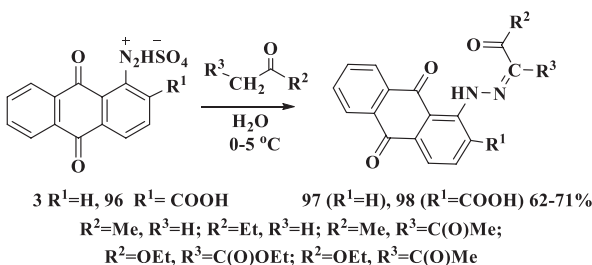


R¹, R² = H, CN, (CH₂)₂, CN, COOMe, COOEt, Ph, C₆H₄Cl, COOH

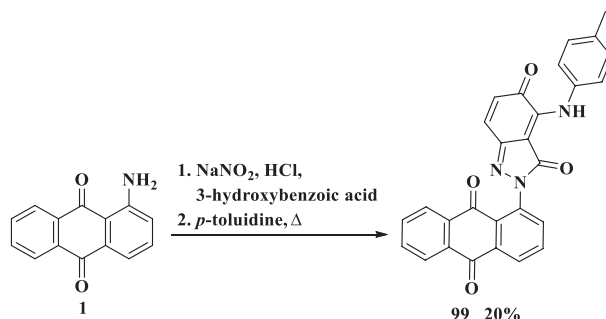
REACTIONS OF DIAZONIUM SALTS OF AMINO-9,10-ANTHRACENEDIONES WITH PRESERVATION OF THE AZO FUNCTION

The azo coupling reaction of diazonium salts of 9,10-dioxoanthracene is one of the key reactions and is widely used in the production of azo dyes [40]. The property of diazotized amino-9,10-anthracenediones to form colored azo coupling products has also been used in analytical methods, in particular for the determination of ascorbic acid [41] and isoniazid [42].

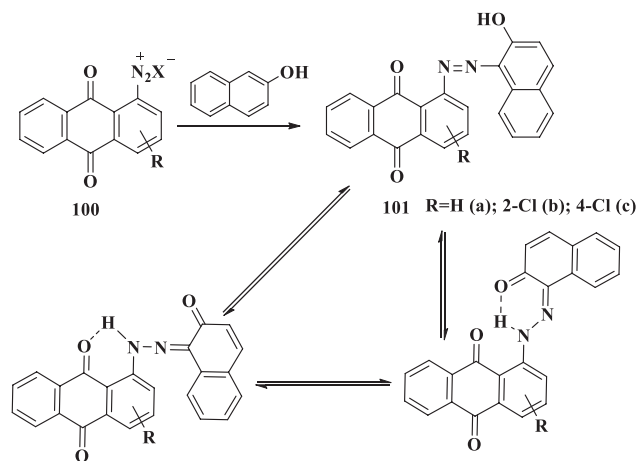
A number of α - and β -carbonyl-containing compounds were successfully used in the modified Jappa-Klingemann reaction with 9,10-dioxoanthracenyldiazonium hydrosulfates **3** and **96** to obtain hydrazone derivatives **97** and **98**, in which acyl and/or alkoxyacetyl groups are present in the ylidene part of the hydrazone fragment [43]. Products **97** and **98** were easily formed with good yields in an aqueous medium by the arylation of carbonyl reagents with freshly prepared diazonium hydrosulfates **3** and **96** under mild temperature and non-base conditions.



The authors in [44] proposed a method for the synthesis of indazolone derivative **99**, which consisted in a sequential two-stage interaction of aminoanthracenedione **1** with 3-hydroxybenzoic acid and *p*-toluidine.

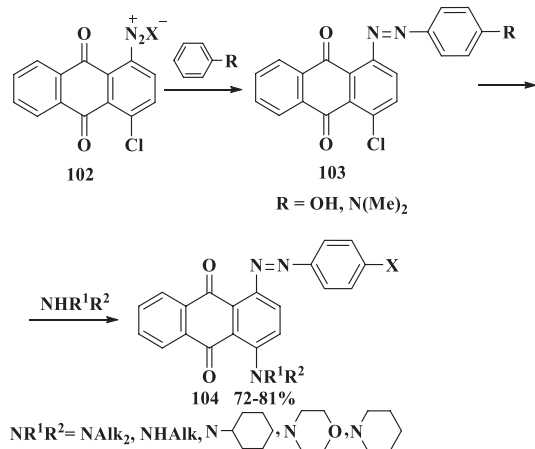


The formation of phenolic and naphthalene derivatives containing the 9,10-dioxoanthracene diazo component occurs quite easily under the conditions of azo coupling of diazonium salts with an aromatic component [45–47]. For the products of azo coupling of diazonium salts **100** with β -naphthol **101** in solutions of dimethyl sulfoxide or chloroform, a tendency to azo-hydrazone tautomerism was found as a result of the *peri*-effect of the carbonyl group [48].

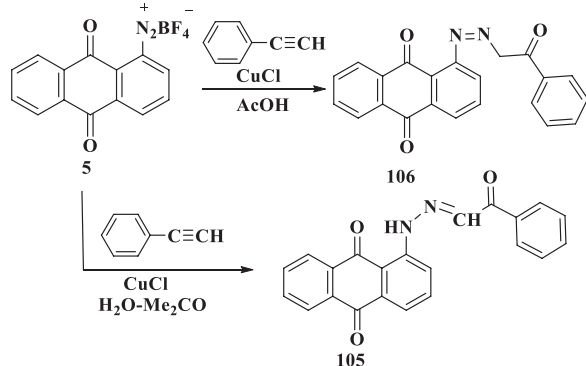


In the above mentioned work, a number of 1-arylaazo-9,10-anthracenedione derivatives **103** with aminoalkyl, aminocarbocyclic and heterocyclic moieties at the position 4 were prepared in sequential reactions of azo coupling of salt **102** and nucleophilic substitution in compounds

103 in a medium of *N,N*-dimethylacetamide at 50–60 °C or *N,N*-dimethylformamide in the temperature range of 60–80 °C.

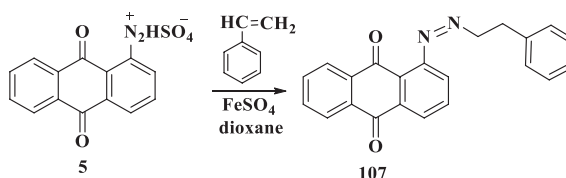


As noted above, the Cu(I)-catalyzed arylation of phenylacetylene by 9,10-dioxoanthracenyldiazonium tetrafluoroborate **5** has its own specificity and can occur with the formation of various reaction products [33]. In particular, it was established that in aqueous acetone azo couplings are realized with the formation of hydrazones of derivative **105**. Instead, isomeric 1-[(2-oxo-2-phenylethyl) diazenyl]anthracene-9,10-dione **106** is formed in the medium of acetic acid or dimethyl sulfoxide.

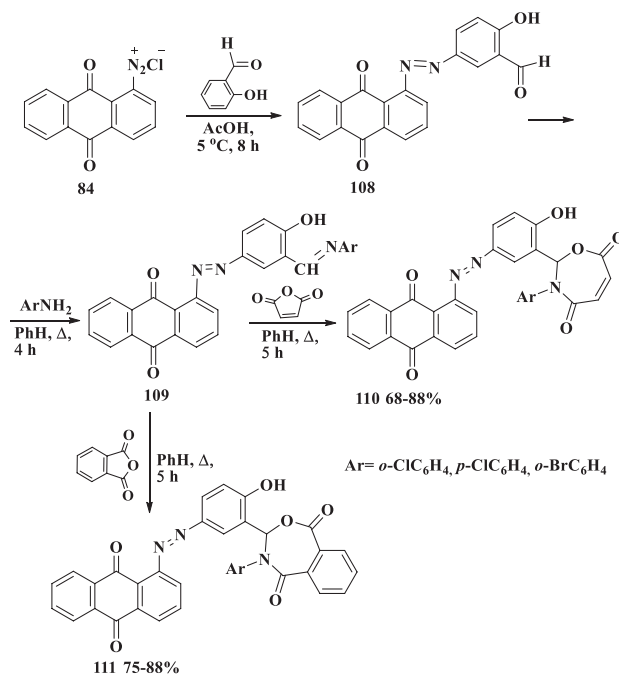


In contrast to the products of a similar reaction in DMSO [32], the arylation of styrene under conditions of a catalytic amount of iron(II)

sulfate in dioxane leads to the formation of azo product **107** [33].

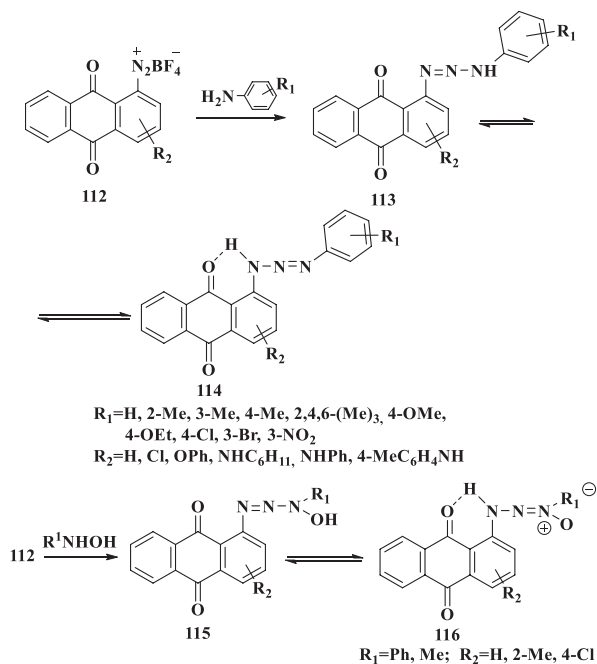


A convenient way of obtaining hybrid structures with 1,3-oxazepinedione **110** and benzo[1,3]oxazepinedione **111** cycles based on the successive transformations of azo coupling product **108** obtained with 9,10-dioxoanthracene-1-ylidiazonium **84** and salicylic aldehyde has been proposed in [49].

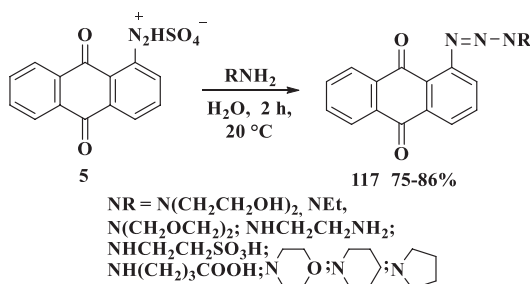


A series of 9,10-anthracenedione triazene derivatives **113** and **115** was obtained by the arylation of the corresponding arylamines and hydroxylamine substituted by salts **112** in the presence of catalytic amounts of AcONa in a DMF medium. The synthesized compounds

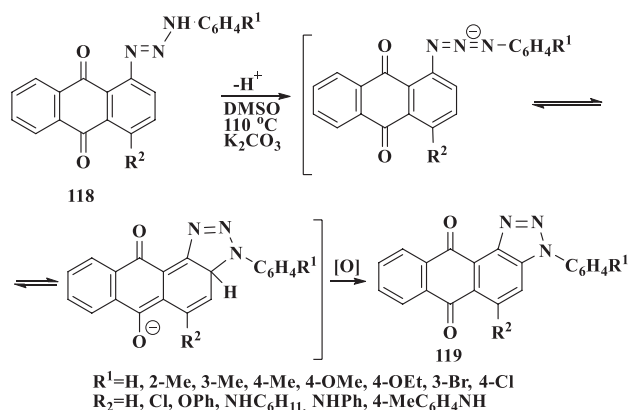
were found to be capable of azo-hydrazone tautomerism [48].



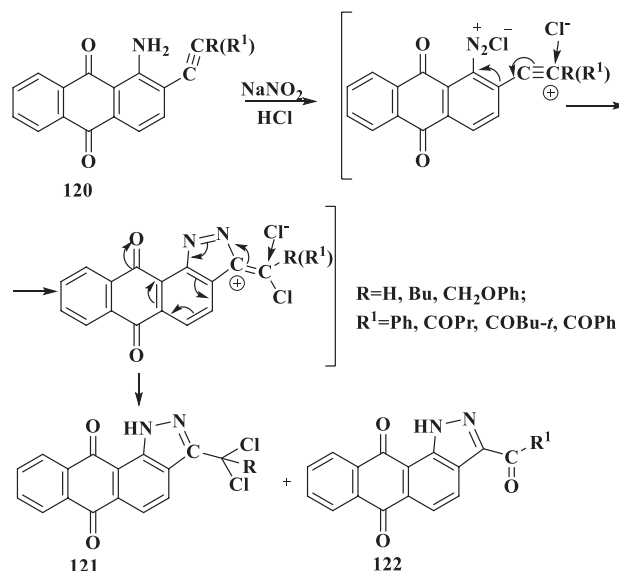
Triazene derivatives with *N*-aminoalkyl fragments **117** were obtained in high yields by the azo coupling of diazonium salt **5** with a number of aliphatic amines [10, 50, 51].



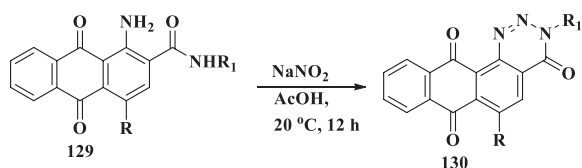
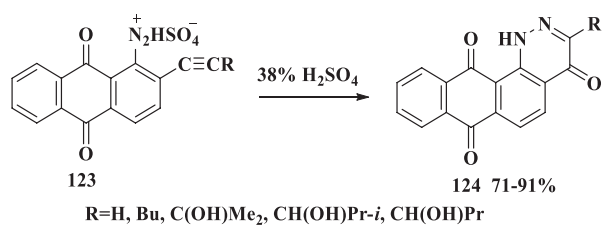
The work [48] describes the synthesis of 1-(aryltriazene)-4-substituted-9,10-dioxoanthracenes **118**, which were cyclized to triazolo-anelated derivatives **119** in dimethyl sulfoxide in the presence of catalytic amounts of potassium carbonate.



The diazotization of acetylene-containing 1-amino-9,10-anthracenediones **120** in the presence of hydrochloric acid leads to the formation of a mixture of annelated pyrazole derivatives **121** and **122**.

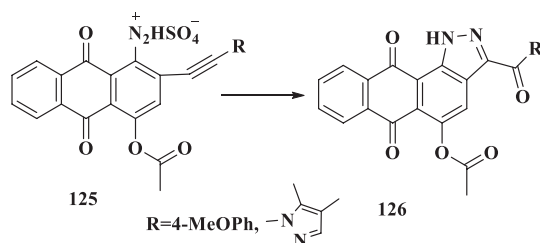


In turn, diazonium sulfates **123** intramolecularly condense under the action of sulfuric acid into naphtho[2,3-*h*]cinoline-4,7,12-(1*H*)-triones **124** [52, 53].

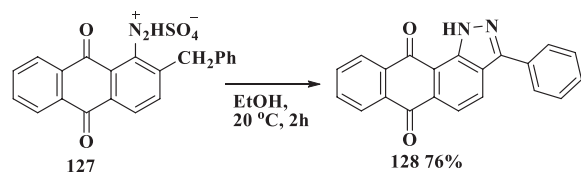


R = R₁ = H; R = H, R₁ = 2-CF₃C₆H₄; R = H, R₁ = 3-MeC₆H₄;
 R = H, R₁ = C₆H₁₁; R = H, R₁ = 3-FC₆H₄; R = H, R₁ = 4-FC₆H₄;
 R = H, R₁ = 3-ClC₆H₄; R = H, R₁ = 4-ClC₆H₄;
 R = H, R₁ = 2-OMeC₆H₄; R = Br, R₁ = H; R = Br, R₁ = 3-FC₆H₄;
 R = Br, R₁ = 2-OMeC₆H₄; R = Br, R₁ = C₆H₁₁; R = Br, R₁ = 4-FC₆H₄;
 R = Br, R₁ = 3-ClC₆H₄; R = Br, R₁ = 4-ClC₆H₄; R = Br, R₁ = 2-CF₃C₆H₄

It was found that compounds **125** with the simultaneous presence of an acetyl fragment at the position 4 of the anthracenedione nucleus and of electron-donating substituents in the alkyne fragment form cyclic derivatives **126** in excellent yields (up to 89%) [29].



3-Phenyl-1*H*-naphtho[2,3-*g*]indazole-6,11-dione **128** was formed in a fairly high yield from 1-diazonium-2-benzyl-9,10-anthracenedione sulfate **127** in ethanol [54].



An efficient synthetic approach [55] for the preparation of a number condensed derivatives of 9,10-anthracenediones, namely anthra[1,2-*d*][1,2,3]triazine-4,7,12(3*H*)-triones **130**, was proposed via the conditions of diazotization intramolecular cyclization reaction of 1-amino-9,10-dioxoanthracene-2-carboxamides **129**.

CONCLUSIONS. Thus, the presented generalized literature data on the known reactions of diazonium salts of 9,10-anthracenedione show their pronounced synthetic potential. Moreover, the preparation of derivatives according to the dediazonation scheme under the conditions of the Sandmeyer, Meerwein, Gomberg – Bachmann – Hay or azo coupling reactions is presented in most of the published works. In turn, the approach associated with the arylation of *S*-nucleophiles is less studied and is limited to the synthesis of only some of their representatives. The works devoted to the arylation of aryl alkynes, arylamines, and carbonyl-containing compounds by diazonium salts with the formation of hydrazone derivatives deserve special attention. The use of 9,10-anthracenyldiazonium salts is no less synthetically significant in the reactions of annelation of triazole, pyrazole, pyridazine and triazinone nucleus.

СИНТЕТИЧНИЙ ПОТЕНЦІАЛ 9,10-АНТРАХІНОНІЛДІАЗОНІЄВИХ СОЛЕЙ

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Вперше узагальнено та систематизовано літературні джерела, які стосуються хімічних перетворень діазонієвих солей 1(2)-аміно-9,10-антрацендіонів. Розкрито потенціал солей 9,10-діоксоантраценілдіазонію як ключових субстратів у процесах одержання різноманітних лінійно-функціоналізованих, ациклічних та гетероциклічних похідних. Проаналізовано основні синтетичні перетворення діазонієвих солей аміно-9,10-антрацендіонів, які реалізуються без збереження азофункції і призводять до утворення продуктів реакцій Зандмеєра, Меєрвейна та Гомберга – Бахмана – Хєя. Висвітлено використання солей 9,10-діоксоантраценілдіазонію або продуктів їхніх трансформацій для одержання гетерилвмісних конденсованих та функціоналізованих похідних.

Ключові слова: діазонієві солі 1(2)-аміно-9,10-антрацендіонів, дедіазоніювання, азосполучення, анелювання, гетерилфункціоналізація

СИНТЕТИЧЕСКИЙ ПОТЕНЦИАЛ 9,10-АНТРАХИНОНИЛДИАЗОНИЕВЫХ СОЛЕЙ

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Впервые обобщены и систематизированы литературные источники, касающиеся химических превращений диазониевых солей 1(2)-амино-9,10-антрацендионов. Раскрыт потенциал солей 9,10-диоксоантраценилдиазония как ключевых субстратов в процессах получения различных линейно-функционализированных, ациклических и гетероциклических производных. Проанализированы основные синтетические преобразования диазониевых солей амина-9,10-антрацендионов, которые реализуются без сохранения азофункции и приводят к образованию продуктов реакций Зандмейера, Меервейна и Гомберга – Бахмана – Хєя. Освещено использование солей 9,10-диоксоантраценилдиазония или продуктов их трансформации для получения гетерилсодержащих конденсированных и функционализированных производных.

Ключевые слова: диазониевые соли 1(2)-амино-9,10-антрацендионов, дедиазонирование, азосочетание, аннелирование, гетерилфункционализация

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