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Review

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Oksana V. Ponomarenko[1*], Svetlana Yu. Panshina[2], Abdigali A. Bakibaev[3], Rahmetulla Sh. Erkasov[4], Madina S. Kenzhebaj[1], Anel' S. Montaeva[1]

[1]*Sh. Ualikhanov Kokshetau University, Kokshetau, Kazakhstan;*
[2]*Karagandy University of the name of academician E.A. Buketov, Karaganda, Kazakhstan;*
[3]*National Research Tomsk State University, Tomsk, Russian Federation;*
[4]*L.N. Gumilyov Eurasian National University, Astana, Kazakhstan*
*(*Corresponding author's e-mail: oksana.ponomarenko.88@mail.ru)*

Glycoluril and Its Chemical Properties

In the chemistry of heterocyclic compounds, bicyclic bisureas — glycolurils, have a special place. Glycolurils are used as a basis for the industrial production of substances that have found application in many areas of human life. The variety of glycoluril derivatives and their properties is primarily due to various substituents in the bicyclic structure. In this review, 2,4,6,8-tetraazabicyclo[3.3.0.]octane-3,7-dione (glycoluril), as the main representative of bicyclic bisureas, its physico-chemical properties, and methods for the synthesis of derivatives based on it are considered. In particular, the main physico-chemical characteristics of glycoluril and the data obtained from its spectral analysis by IR, NMR spectroscopy and X-ray diffraction analysis are presented and discussed. The paper briefly outlines the known methods for the synthesis of glycolurils and related compounds, also highlights the chemical properties of glycoluril and its derivatives, as well as the ways to modify them. Coordination compounds based on N-alkylglycolurils as ligands are briefly considered. The reaction products of N-halogenation and N-acylation of glycolurils are presented and discussed. Reactions for obtaining phosphorus-, nitro- and nitroso derivatives of glycolurils; alkylation methods, Mannich reactions, thionization, alkaline hydrolysis and reduction reactions at the carbonyl group of glycolurils are also shown. There is a discussion of the macromolecules formation in the condensation reaction of glycoluril with formaldehyde as precursors for the synthesis of cucurbit[n]urils.

Keywords: glycoluril, tetraacetylglycoluril, tetramethylglycoluril, tetrachloroglycoluril, dinitrosoglycoluril, phosphorus derivatives of glycoluril, thioglycoluril.

Contents

Review Plan

Inclusion and Exclusion Criteria: This review is devoted to bicyclic bisureas, in particular glycoluril and its derivatives. The physico-chemical properties of glycoluril and methods for its modifications are described.

The review data mostly cover the publications from 1994 to 2021. However, there are older references from the period 1963–1986, as well as references to primary research sources dated on 1878, 1907, 1889 are also cited.

To write this review, we used directly our own research, as well as additional sources from databases such as Scopus, Web of Science and other online scientific search engines. The keywords used for the search were "Halogenation of Glycoluril", "Acylation of Glycoluril", "Phosphorylation of Glycoluril", "Nitration and Nitrosation of Glycoluril", "Alkylation of Glycoluril", "Thionization of Glycoluril", "Hydrolysis of Glycolurils", "Reduction of Carbamide Groups", "Trioxohexaazapropellanes". The resultant data are described in this article. No statistical methods were used in this review.

Introduction

Bicyclic bisureas, in particular 2,4,6,8-tetraazabicyclo[3.3.0.]octane-3,7-dione (glycoluril **1a**) (Fig. 1) and its derivatives occupy a special place in the chemistry of heterocyclic compounds. Substances based on glycolurils are produced on a large scale. Glycoluriles are used as components of disinfectants, pharmaceuticals [1, 2], stabilizers in polymer synthesis [3, 4], explosives and their components [5–11], etc. Recently, a new direction in the chemistry of glycolurils has been developed, namely, the creation of macrocyclic compounds with unique controllable properties. Cucurbit[n]urils, bambus[n]urils, tiara[n]urils, "molecular clamps" and supramolecular systems have been synthesized on the basis of glycoluril and its derivatives [12–19].

Glycoluril-based supramolecular systems have been proposed as materials with the properties of "molecular recognition", excipients — prolongators for drugs [20–22], components of semiconductor compositions [23] and molecular sensors for the analysis of amphiphilic components [24–27]. In addition, it is known [27–29], that glycolurils are low-toxic and do not exhibit carcinogenic properties.

1 Glycoluril as the main representative of the bicyclic bisureas

Glycoluril **1a**, as the first representative of bicyclic bisureas, was synthesized in the second half of the 19th century, and at the same time, its bicyclic structure, similar to urea, was determined [30, 31]. However, it has recently been found [32] that the glycoluril molecule **1a** is not planar and has an angle between two imidazolidinone fragments equal to 124.1º and nitrogen atoms are located equidistantly from each other. Hydrogen atoms at methine carbons are *cis*-oriented. Imidazolidinone rings are almost flat, but have a slight deviation of the C=O groups from the mean plane [32] (Fig. 1).

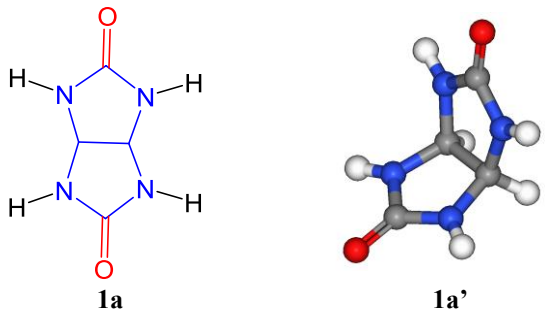


Figure 1. Structural formula of glycoluril **1a** and its spatial configuration in the crystal **1a'**
Adapted and redrawn from Ref. [32] with permission from Springer Nature

Glycoluril **1a** is a polyfunctional compound, molecule **1a** of which contains two carbamide fragments (Fig. 2). These fragments (4 donor NH-groups and 2 acceptor C=O-groups) determine the chemical properties of substance **1a**.

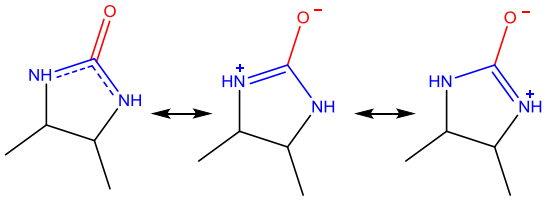
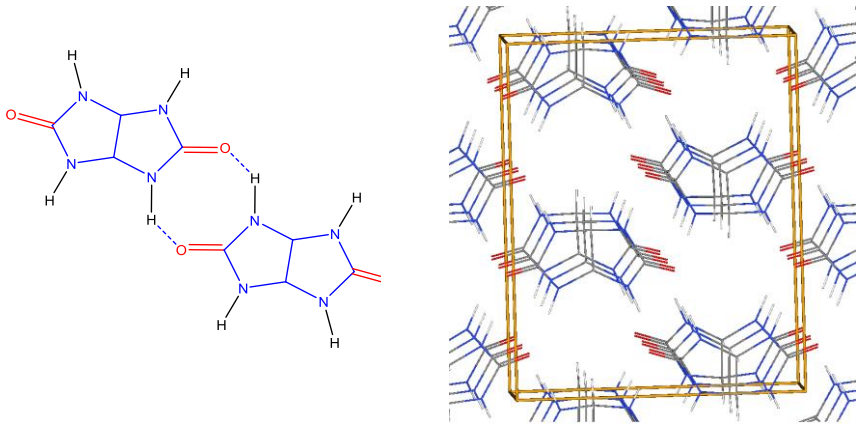


Figure 2. Resonance structures of the carbamide fragment in the glycoluril molecule **1a**

Substance **1a** is white crystals with strong intermolecular hydrogen bonds (Fig. 3). Strong internal interactions are responsible for the high melting point (360 °C with decomposition) and the low solubility of glycoluril **1a**.



a **b**

Figure 3. Hydrogen bonds in glycoluril crystals **1a**:
a — type of formation of hydrogen bonds; **b** — packing diagram of glycoluril **1a** in a crystal.
Adapted and redrawn from Ref. [32] with permission from Springer Nature

Glycoluril **1a** exists in two polymorphic forms [32] which can crystallize in water simultaneously. The effect of polymorphism of glycoluril **1a** significantly affects the physico-chemical properties. In solutions, this effect is leveled due to the equivalent effect of the solvent on the crystal structure of **1a** and does not affect the reactivity. Physico-chemical characteristics of glycoluril **1a** [33, 34] are presented in Table.

T a b l e

Physical and chemical characteristics of glycoluril 1a [33, 34]

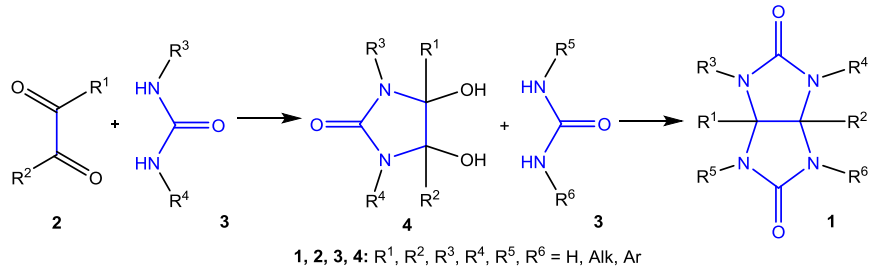
Parameter	Value
Melting point	360°C (decomp.)
Insoluble in:	haloalkanes, alcohols, ketones, ethers
Weakly soluble in	DMSO, DMF, Ac_2O, H_2O, acids
IR spectrum, ν, cm^{-1}:	3209 (NH), 1675 (C=O).
^{1}H NMR (DMSO-d_6, δ, ppm):	5.24 (s. 2H, CH), 7.16 (s. 4H, NH)
^{13}C NMR (DMSO-d_6, δ, ppm):	160.3 (C=O), 64.6 (CH)

Given the specific limited solubility of glycoluril **1a** (Table), such solvents as DMSO-d_6 and D_2O are most commonly used for the identification of glycolurils by NMR methods [35].

When analyzing glycoluril **1a** in D_2O, the chemical shift of NH groups in the ^{1}H NMR spectrum is most often hidden due to deuterium exchange. When using the DMSO-d_6 solvent, the molecule **1a** in the ^{1}H NMR spectrum is shown by two chemical shifts at 5.24 ppm and 7.16 ppm, which correspond to the signals of the CH-CH and NH groups. In the ^{13}C NMR spectrum (DMSO-d_6) the structure of glycoluril **1a** is shown by peaks at δ 64.6 ppm and δ 160.3 ppm which correspond to CH-CH-carbons and carbonyl (C=O) carbons, respectively [35].

The equivalence of carbon and hydrogen atoms in the bicyclic structure indicates the spatial symmetry of the glycoluril molecule **1a**.

With the development of the chemistry of glycolurils many methods for their synthesis were created [36, 37]. The most convenient method for preparing glycolurils **1a** is the reaction of ureas **3** and their derivatives with *α*-dicarbonyl compounds **2** (Scheme 1).

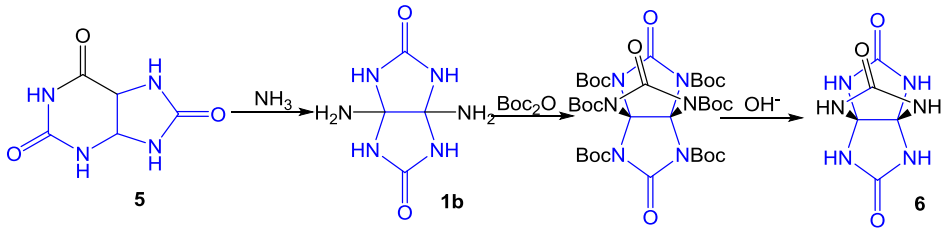


Scheme 1. Method for the synthesis of glycolurils **1** [36]

According to the mechanism of *α*-ureidoalkylation, the products of the first stage of condensation of ureas **3** and glyoxal **2** are 4,5-dihydroxyimidazolidin-2-ones **4** (DHI) – these are reaction intermediates in the further formation of glycolurils **1**. The well-known DHI **4** series and their analogues are actively used in reactions with various urea derivatives. Thus, this approach is the second method for the synthesis of various types of glycolurils **1** and their analogs (Scheme 1) [36, 37].

In accordance with the described method (Scheme 1), glycolurils unsubstituted at nitrogen atoms, glycolurils with substitution at C_1-C_5 atoms, *2-N*-substituted glycolurils, *2,4,6-N*-trisubstituted glycolurils, *2,6-N*-di-, *2,8-N*-di-, *2,4,6,8-N*-tetrasubstituted glycolurils were obtained [36, 37].

1,5-Diaminoglycoluril **1b** can be obtained from uric acid **5** by oxidation at minus 5 ºC in the presence of ammonia (Scheme 2). Based on 1,5-diaminoglycoluril **1b**, a group of Korean scientists developed a method for obtaining a tricyclic derivative of glycoluril with six NH-groups — 3,7,10-trioxo-2,4,6,8,9,11-hexaaza[3.3.3]propellane **6** (Scheme 2) [38, 39].



Scheme 2. The synthesis of 3,7,10-trioxo-2,4,6,8,9,11-hexaaza[3.3.3]propellane **6** [39]

Glycoluril **1a** is an active *n*-nucleophile and a significantly inactivated *p*-nucleophile. The presence of (NH–C=O) bonds with an electron-withdrawing carbonyl group makes it a less reactive base. This explains the difficulty of protonation of NH-groups, as well as the tendency for the decomposition of products formed as a result of electrophilic attack on the nitrogen atom.

In addition, the weak electrophilic properties of the carbonyl group are explained by the conjugation of two lone pairs of electrons from nitrogen atoms, which compensate for the electron-withdrawing effect of the carbonyl group. However, substance **1a** easily enters into reactions of *N*-alkylation, *N*-acylation, *N*-halogenation, *N*-nitration, *N*-nitrosation, *N*-hydroxyalkylation, etc [40].

Glycolurils form complex compounds [32]. In their structures, oxygen and nitrogen atoms are the most probable coordination centers for complexation. However, coordination through nitrogen atoms, as a rule, is sterically difficult due to its predominantly pyramidal structure, especially since this center has a reduced electron density compared to oxygen [32]. *N*-alkylglycolurils are polydentate ligands and can perform both monodentate and bidentate bridging functions with metals, with bonding through C=O groups. The bonding type depends on the coordination number of the metal atom (Fig. 4).

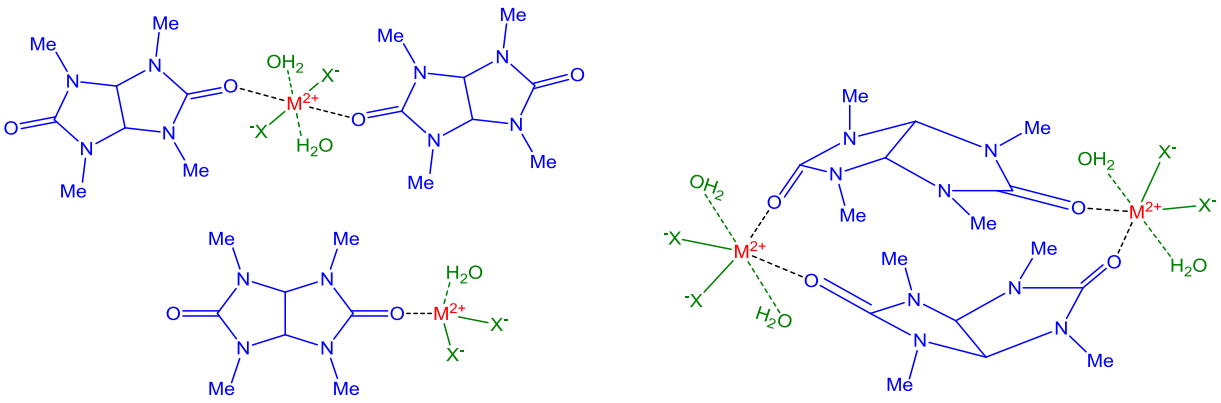


Figure 4. Coordination Options for *N*-alkylglycolurils

Thus, the structure of coordination compounds based on *N*-alkylglycolurils and salts of *d*- and *f*-metals such as Mn, Pr, Sm, Eu, and Gd were studied by X-ray diffraction analysis [32]. In all these cases, coordination compounds based on *N*-alkylglycoluril represent a centrosymmetric binuclear complex of a metal cation, where two molecules of *N*-alkylglycolurils are ligands (Fig. 5).

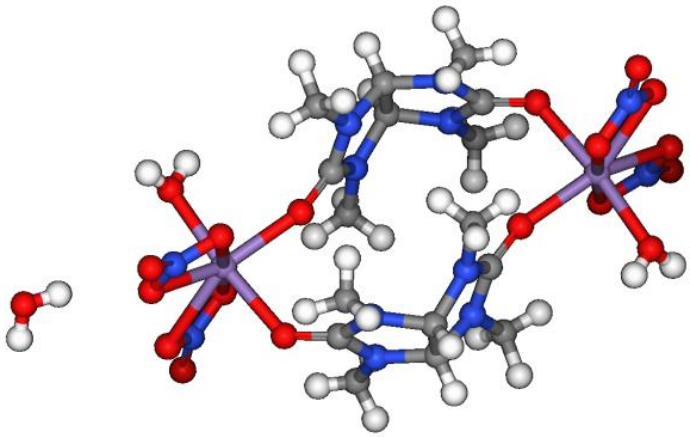


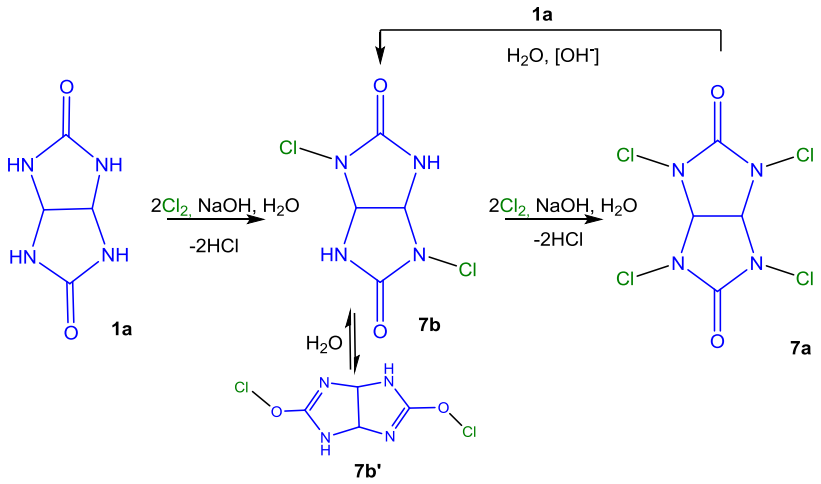
Figure 5. Centrosymmetric binuclear complex based on *N*-alkylglycoluril [41]

Derivatives of glycoluril with different numbers of substituents at *N*-, *C*-atoms can be synthesized both by a single-stage reaction and with step-by-step modification of the original glycoluril **1a**. The synthesis and study of the chemical properties of bicyclic bisureas allows us to reach new classes of nitrogen-containing heterocyclic compounds with various practically useful properties. Examples are such polycyclic condensed systems as cucurbit[n]urils, bambusurils, thiaraurils, "molecular clamps" [12-19], building blocks of which are glycolurils **1** (Scheme 1).

2 Halogenated glycolurils

Halogenated derivatives of glycoluril are used as oxidizers, halogenating agents, disinfectants, bleaches and detergents. The bactericidal activity of these compounds depends on the type of halogen. Thus, 2,4,6,8-tetrachloro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (tetrachloroglycoluril) **7a** and 2,6-dichloro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (dichloroglycoluril) **7b** are used as active chlorine atom carriers for algae control in industrial water and wastewater treatment [42].

In organic chemistry, tetrachloroglycoluril **7a** is used as a mild chlorinating agent in organic synthesis and is convenient because it has greater thermal stability than other known chloramides. The synthesis of tetrachloroglycoluril **7a** proceeds by the interaction of glycoluril **1a** and gaseous chlorine in a slightly acidic medium (Scheme 3). Substance **7a** is insoluble in water and reacts explosively with DMSO [42].

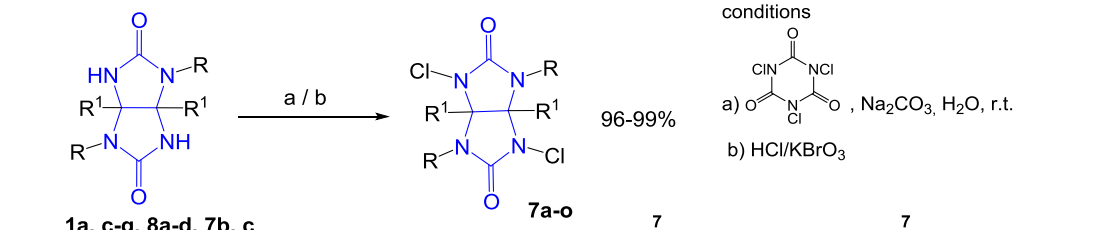


Scheme 3. The synthesis of tetrachloroglycoluril **7a** and dichloroglycoluril **7b** [42]

The highest yields of tetrachloroglycoluril **7a** were obtained in the pH range 3−7. It was shown that in the presence of an alkaline catalyst tetrachloroderivative **7a** enters into equilibrium hydrolysis with glycoluril **1a** on *N*-chlorine bond with a quantitative yield of dichloroglycoluril **7b** [43]. Dichloroglycoluril **7b** can also be selectively obtained by adjusting the amount of chlorinating reagent [43].

It is supposed [41] that dichloroglycoluril **7b** exists as two tautomeric structures **7b** and **7b'** (Scheme 3). The authors [41] attribute this assumption to the presence of three chemical shifts δ 72.8, 64.6 and 62.8 ppm of carbon atoms of the CH-CH groups and the absence of C=O carbonyl or isourea carbon signals in the ^{13}C NMR (D_2O) spectra. It was also found that in the study of crystalline dichloroglycoluril **7b** by IR spectroscopy, the IR spectrum contained absorption bands of carbonyl groups (1740 cm^{-1}) and bands corresponding to vibrations of ether bonds (1250 and 1100 cm^{-1}), which were absent in the IR spectrum of tetrachloroglycoluril **7a**.

A modified method for the preparation of chlorine derivatives of glycolurils **7b, d–j** at room temperature using a safe and easily processed reagent − trichloroisocyanuric acid (Scheme 4) without the use of any surfactant was proposed [44].



1a: R = H, R^1 = H
1c: R = H, R^1 = Me
1d: R = H, R^1 = Et
1e: R = H, R^1 = Ph
1f: R = H, R^1 = 4-BrC_6H_4 / 3-BrC_6H_4
1g: R = H, R^1 = 4-ClC_6H_4 / 3-ClC_6H_4

8a: R = Bu^t, R^1 = H
8b: R = $PhCH_2$, R^1 = H
8c: R = $PhCH_2$, R^1 = Ph
8d: R = Bu^t, R^1 = Ph
7b: R = Cl, R^1 = H
7c: R = Cl, R^1 = Ph

7
a: R = Cl, R^1 = H (b)
b: R = H, R^1 = H, (a / b)
c: R = Cl, R^1 = Ph (b)
d:R = H, R^1 = Me (a)
e: R = H, R^1 = Et, (a)
f: R = H, R^1 = Ph, (a)
g: R = H, R^1 = 3-BrC_6H_4 (a)
h: R = H, R^1 = 4-BrC_6H_4 (a)

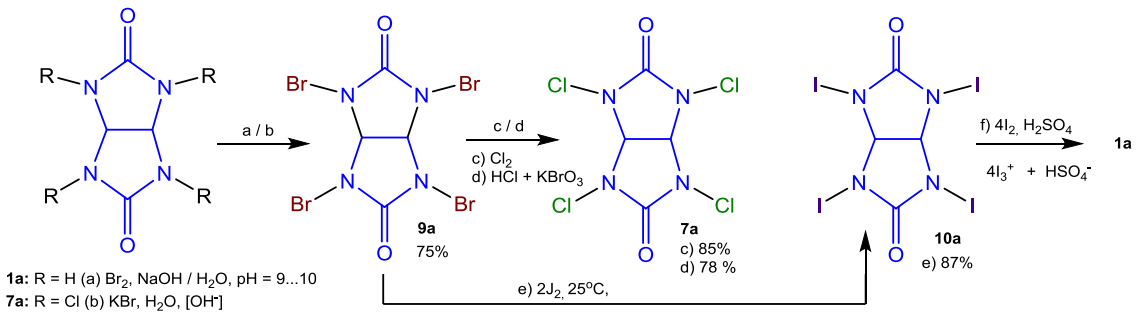
7
i: R = H, R^1 = 3-ClC_6H_4 (a)
j: R = H, R^1 = 4-ClC_6H_4,(a)
k: R = t-Bu, R^1 = H (b)
l: R = $PhCH_2$, R^1 = H (b)
m: R = t-Bu, R^1 = Ph (b)
n: R = $PhCH_2$, R^1 = Ph(b)
o: R = Cl, R^1 = Ph (b)

Scheme 4. A modified method for the preparation of chlorine derivatives of glycolurils

The resistance of dichloroglycoluril **7a** to the action of oxidizing agents ($KBiO_3$) made it possible to develop a preparative method for the preparation of *N*-chloroderivatives of glycolurils **7a–c, k–o** with practically quantitative yields [41]. Thus, bicyclic bisureas **1a–f, 8a–d, 7b, c** were subjected to oxidative chlorination with the HCl/$KBiO_3$ system to obtain **7a–c, k–o** (Scheme 4).

Glycoluril **1a** also reacts with molecular bromine in an alkaline medium to form tetrabrominated product **7a** (Scheme 5). Tetrabromoglycoluril **7a** has oxidizing properties and is used as additives to bactericidal, bleaching and detergents and is used as brominating agents or initiators of radical processes [43]. So, the ox-

idizing ability of halogens and hypohalides is highly dependent on the acidity of the medium, the authors [45, 46] studied interconversions in a series of *N*-halogen derivatives of glycolurils.



Scheme 5. Interconversions in a series of *N*-halogen derivatives of glycolurils

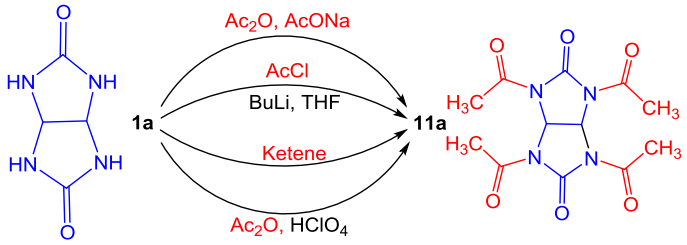
Based on spectral data and quantum chemical calculations, the authors of [47] determined the probability that the dissolution of tetraiodoglycoluril **8a** in sulfuric acid can lead to the formation of the triodione cation I^{3+} together with iodine-containing sulfate ($IOSO_3H$). The authors tried to prepare an I^{3+} solution by the reaction of tetraiodoglycoluril **8a** with iodine in sulfuric acid.

N-fluorine derivatives of glycolurils have not yet been obtained.

3 Acylderivatives of glycoluril

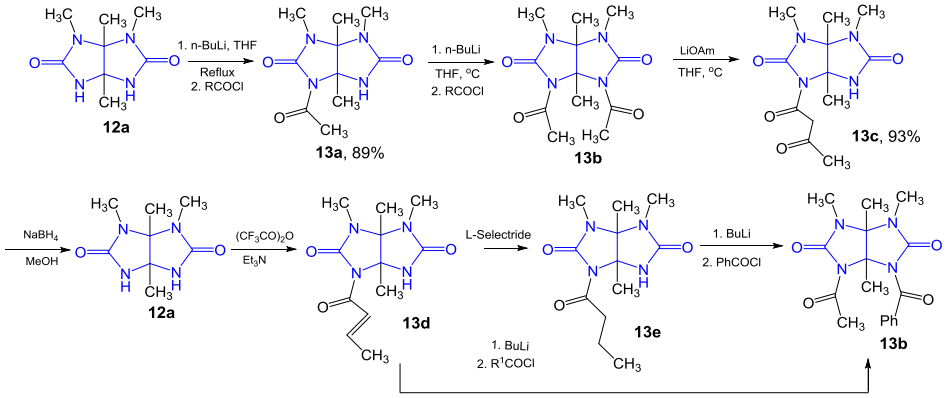
The first reports on the acetylation reactions of glycoluril **1a** with acetic anhydride to form 2,4,6,8-tetraacetyl-2,4,6,8-tetraazabicyclo[3,3,0]octane-3,7-dione (tetraacetylglycoluril) **11a** date back to the end 19th early 20th century [34].

In the development of research, it was found that the best yields of compound **11a** were achieved using catalysts (Scheme 6), [34] especially the highest yield (up to 85 %) of tetraacetylglycoluril **11a** was achieved with chloric acid.



Scheme 6. Acetylation of glycoluril **1a** in the presence of various catalysts [34]

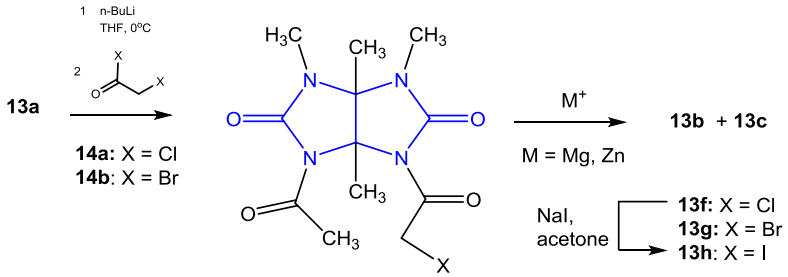
More recently, Cow Ch.N. et al. in a series of their studies [48–50] studied the reactions of *N*-acylation of the tetramethylderivative of glycoluril **12a** with further transformations (Scheme 7).



Scheme 7. The reactions of *N*-acylation of the tetramethylderivative of glycoluril **12a** [34]

Intramolecular *N*-*C*-transacetylation of *syn*-diacetylglycoluril **13b** by the action of lithium amylate allowed the author [51] to obtain selectively difficult-to-access *N*-acylglycolurils **13b–e** (Scheme 7). Structural features of the obtained **13b–e** compounds were determined by X-ray diffraction analysis.

Through the intermediate acylhalogenation of glycoluril **13a** with haloacylhalides **14a, b** followed by dehalogenation of *α*-haloacylglycolurils **13f–h** under the action of metals, there was carried out the synthesis of enolates [51] which underwent further condensation with another acetyl group (Scheme 8).

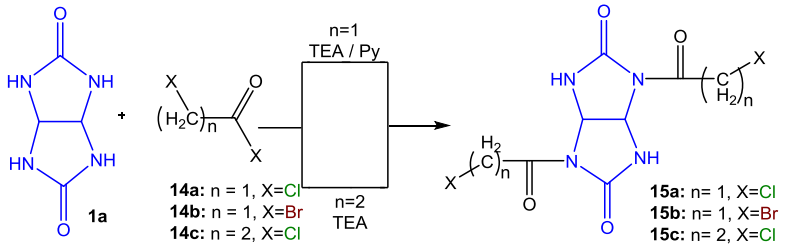


Scheme 8. Interacylation of glycolurils [34]

In the preparation of chloroacetyl derivative **13f** (42 % yield), no side reactions, such as S_N2 substitution, were observed. Bromoacetylglycoluril **13g** was similarly obtained in 44 % yield using bromoacetyl bromide **14b**. And the iodoacetyl compound **13h** was synthesized directly from glycoluril **13f** by reaction with NaI in acetone according to the general method of iodoacetylation, the resulting sodium chloride salt precipitated during the reaction [34].

Under the action of a metal atom, glycolurils **13f–h** eliminated the halogen atom and the main product of this reaction (Scheme 8) was diacetylglycoluril **13b**. When the *non*-activated Mg or Zn powder was combined with chloroacetyl glycoluril **13f** or with bromoacetyl adduct **13g** the highest yields of acetoacetate adduct **13c** were observed. It is possible that the inefficiency of the reaction is due to the poor selectivity of the metal with respect to the carbonyl groups of the substituent rather than the carbonyl groups of glycoluril **13a**. Iodoacetyl glycoluril **13h** proved to be very unstable for further reactions with it [34].

In order to expand the preparative possibilities of the *N*-acylation reactions of glycoluril **1a**, interactions **1a** with haloacylhalides **14a–c**, in particular with 1-bromoacetyl bromide **14b**, 1-chloroacetyl chloride **14a** and 3-chloropropanoic acid chloride **14c** were investigated (Scheme 9) [52].

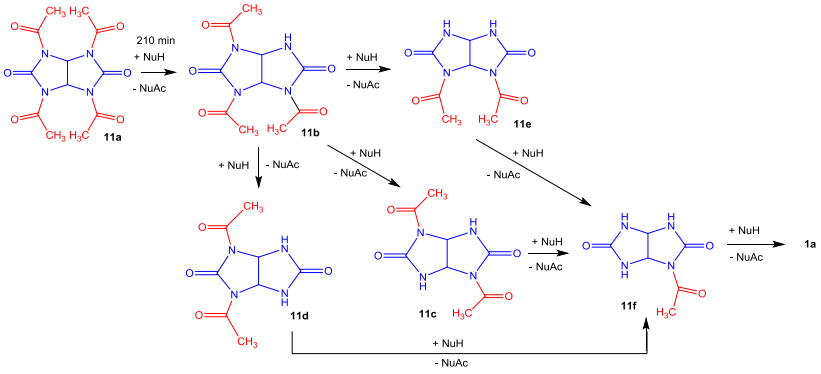


Scheme 9. *N*-haloacylation reactions of glycoluril **1a** [52]

It was shown that the reaction of glycoluril **1a** with 1-bromoacetyl bromide **14b** resulted in the formation of *bis*-acetylbromoglycoluril **15b** (yield 78 %) (Scheme 9). Under the action of 1-chloroacetyl chloride **14a** on glycoluril **1a** *bis*-acetylchloroglycoluril **15a** (yield 68 %) was formed, while using 3-chloropropanoic acid chloride **14c**, *bis*-chloropropionylglycoluril **15c** was obtained in 50 % yield.

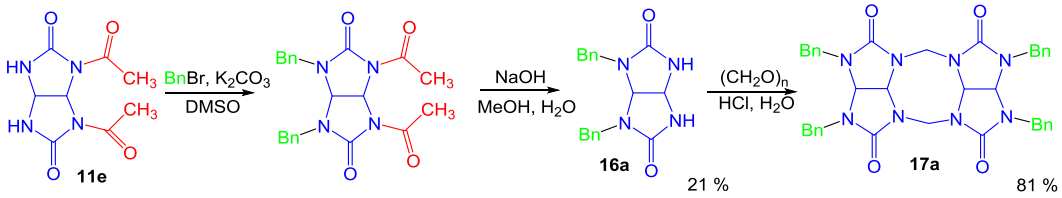
It was shown that, despite an 8-fold excess of reagents, the authors [52] failed to obtain any tetracylhalides of glycoluril **1a** under the studied reaction conditions.

It is known that tetraacetylglycoluril **11a** undergoes hydrolysis processes, which have been studied in detail at room temperature, at pH =10 in an aqueous-alcoholic medium. Under these conditions, tetraacetylglycoluril **11a** is deacetylated stepwise to form a series of *N*-acetylglycolurils **11b–f** and final glycoluril **1a** [53] (Scheme 10). In the work [53], the directions of formation of diacetylglycolurils **11c, e** under the action of urea **3a** were proposed.



Scheme 10. The hydrolysis processes of tetraacetylglycoluril **11a** [53]

The authors of [54] successfully used the propensity to hydrolyze tetraacetylglycoluril **11a** to obtain sterically difficult-to-reach *N*-benzylglycoluril **16a** and dimer **17a** (Scheme 11). This aspect was realized through the formation of *syn*-diacetylglycoluril **11e**, where acetyl groups were used as protecting groups, which are further hydrolyzed for subsequent reactions.



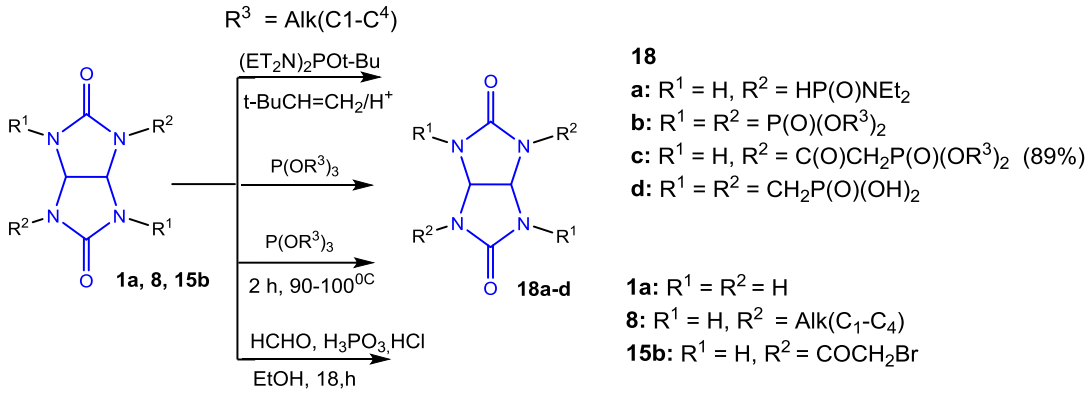
Scheme 11. The synthesis of *N*-benzylglycoluril **16a** and dimer **17a** [54]

The *N*-acetylating properties of tetraacetylglycoluril **11a** in reactions with primary aliphatic and aromatic amines were studied in detail; also a new mechanochemical method for the synthesis of some *N*-acetylamides was proposed [55]. In addition, the possibility of using **11a** as a reagent was demonstrated in separate examples of *O*-acetylation [56].

4 Phosphorus derivatives of glycoluril

Recently, the range of information on phosphorylation reactions of 2,4,6,8-tetraazabicyclo[3.3.0.]-octane-3,7-dione (glycoluril **1a**) has been expanding [57, 58]. Thus, there was investigated the transamidation reaction of glycoluril **1a** with tetraethyldiamido-*tert*-butyl phosphite [59] which resulted in the formation of glycoluril-substituted diethylamido-*tret*-butyl phosphite **18a** (Scheme 12).

The patent [60] describes in detail flame retardants — *N*-phosphorylated derivatives of glycoluril **18b** and methods for their preparation based on *N*-alkyl derivatives of glycolurils **8** (Scheme 12).

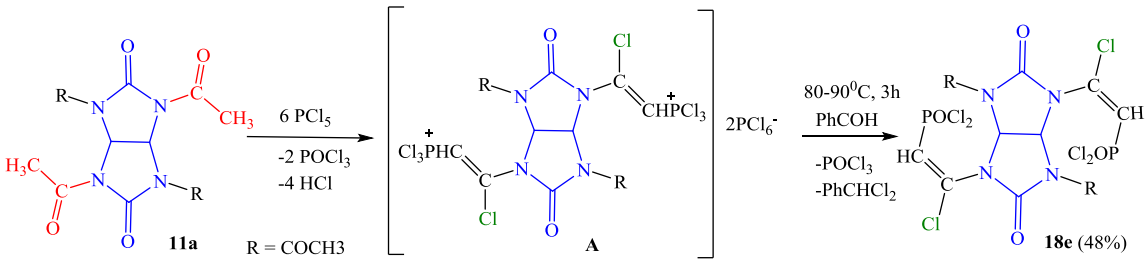


Scheme 12. The synthesis of phosphorus derivatives of glycoluril [57]

The authors of [61] carried out the acid hydrolysis of diphosphonate **18c** which was synthesized from *bis*-bromoacetylglycoluril **15b**. Hydrolysis of glycoluril **18c** leads to the corresponding diphosphonic acid.

Tetrakis(methylene phosphoric acid)glycoluril **18d** was used as an efficient catalyst for the synthesis of pyrazole-5,10-dione derivatives [62]. Substance **18d** was obtained in the "One-pot" synthesis by *N*-peralkylation of glycoluril **1a** with paraformaldehyde and phosphorous acid in refluxing ethanol (Scheme 12).

Diphosphonic complex of terraacetylglycoluril **18e** was obtained by the reaction of phosphorylation of tetraacetylglycoluril **11a** with phosphorus pentachloride (Scheme 13) [57].

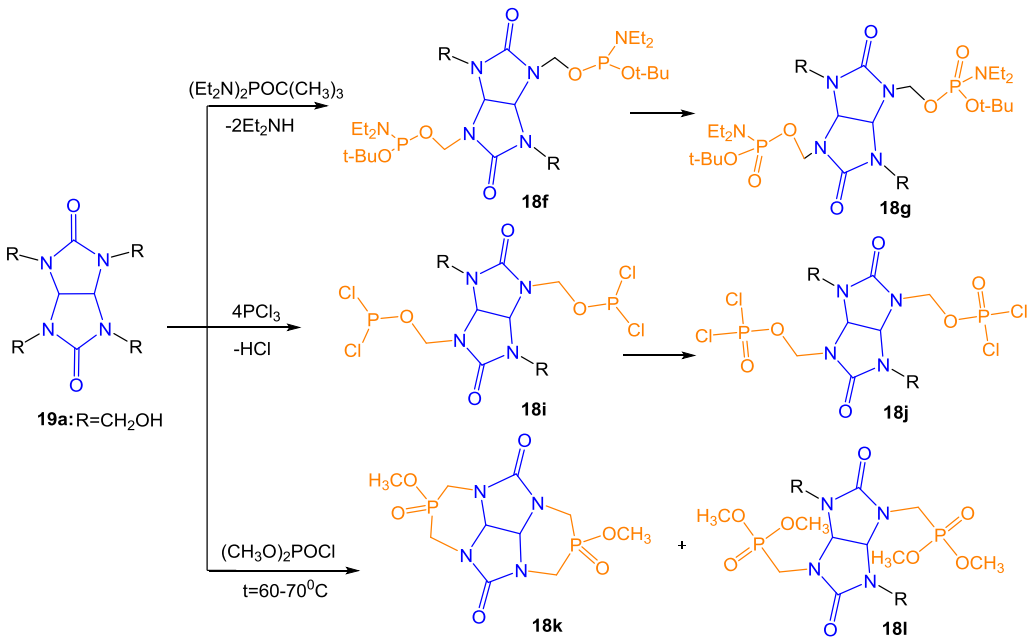


Scheme 13. The reaction of phosphorylation of tetraacetylglycoluril **11a** [57]

Probably the reaction (Scheme 13) proceeds through the addition of phosphorus pentachloride to the oxygen atom of the acetyl group **11a**, with the formation of complex **A**, which further decomposes to the product **18e**.

The phosphorylation reaction of tetra(hydroxymethyl)glycoluril **19a** with tetraethyldiamdo-*tert*-butylphosphite resulted in the formation of the oily product 2,6-di-(*N*-diethylamidomethylolphosphato)-glycoluril **18g** via the formation of intermediate **18f** (Scheme 13) [59]. Direct interaction of **19a** with phosphorus trichloride led to the isolation of a yellow crystalline substance, namely 2,6-di-(*N*-methylchlorophosphato)-4,8-chloromethylglycoluril **18i**. Glycoluril **18i** underwent oxidation of phosphorus fragments to the pentavalent state with the formation of compound **18j** (Scheme 14).

The reaction of tetrahydroxymethylglycoluril **19a** in absolute benzene with two equivalents of dimethoxychlorophosphate and pyridine as a hydrogen chloride acceptor resulted in the formation of a mixture of products **18k** and **18l** (Scheme 14) [59].

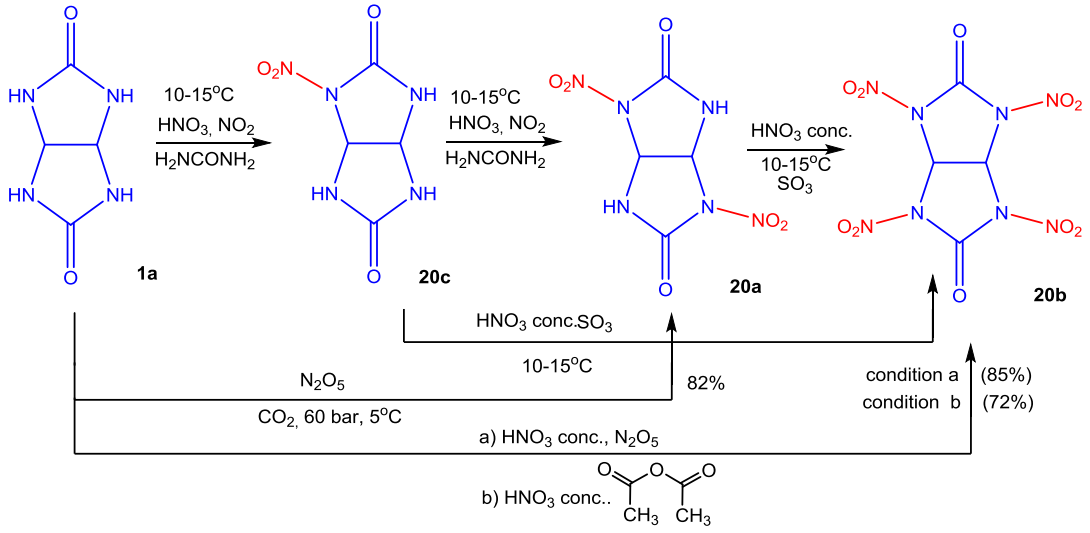


Scheme 14. The phosphorylation reaction of tetra(hydroxymethyl)glycoluril **19a** [59]

A comprehensive analysis of chemical shifts in the ^{31}P and ^{13}C NMR spectra of glycolurils and other phosphorus derivatives of bicyclic bisureas was carried out [59].

5 Nitro- and nitrosoderivatives of glycoluril

N-nitro- and *N*-nitroso derivatives of glycolurils have long attracted the attention of researchers, as they have found applications as explosives and pore-forming agents [6]. These substances, in particular 2,6-dinitro-2,4,6,8-tetraazabicyclo[3.3.0.]octane-3,7-dione (dinitroglycoluril) **20a**, were first discovered in the 1880-s [63]. And 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3.3.0.]octane-3,7-dione (tetranitroglycoluril) **20b** was first obtained only in the 1970s by the French scientist Boileau [5, 64]. Further, the reactions of formation of *N*-nitroglycolurils were studied in detail [65]. Thus, in the reactions of *N*-nitration of glycoluril **1a**, the *anti*-*N*-dinitro-substituted product **20a** was mainly formed, but monosubstituted glycoluril **20c** was also present. Nitration of **20c** with a mixture of nitric acid and sulfuric anhydride can lead to the formation of tetranitroglycoluril **20b**. Tetranitroglycoluril **20b** was also formed by *N*-nitration of dinitroglycoluril **20a** with a mixture of nitric acid and nitric anhydride at 15 °C (Scheme 15).



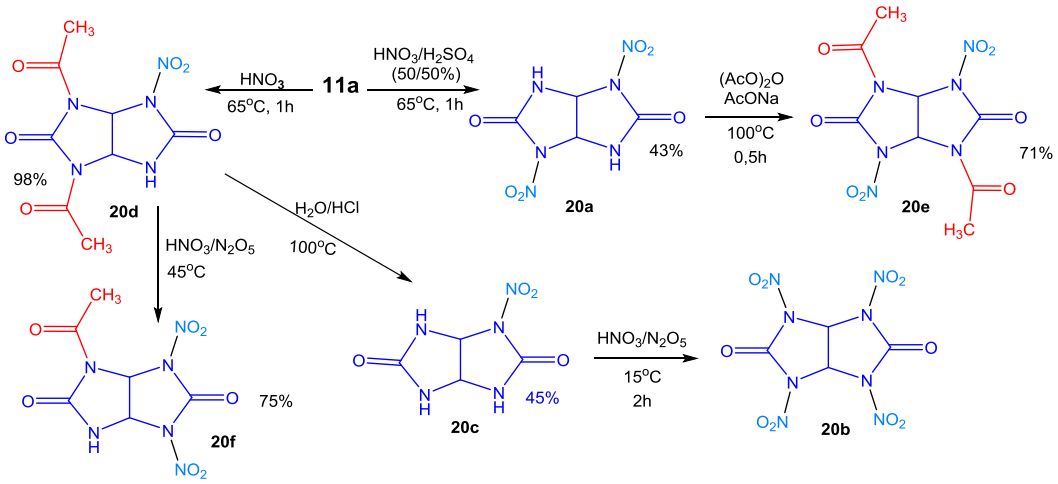
Scheme 15. The synthesis of *N*-tetranitroglycoluril **20b**

Dinitroglycoluril **20a** is synthesized selectively by *N*-nitration of glycoluril **1a** with concentrated nitric acid in the presence of urea **3a** or urea nitrate. The autoclave method [9] of synthesizing **20a** with an 82 % yield is known. It proceeds under conditions of liquid CO_2 gas at a pressure of 60 bar and a temperature of 5 °C using nitrogen pentoxide as a nitrating agent [9, 65, 66] and acetic anhydride (72 %) (Scheme 15) [67–69].

In [70], the solubility of tetranitroglycoluril **20b** in acetone, methanol, ethanol, ethyl acetate, nitromethane, and chloroform was measured in the temperature range from 295–318 K by the gravimetric method.

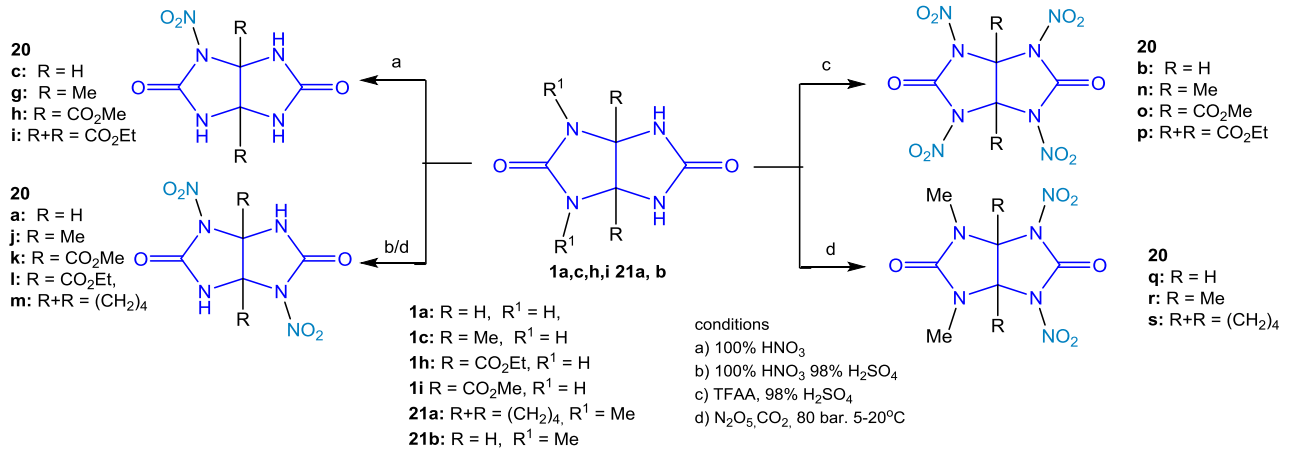
A number of *N*-nitroderivatives of glycoluril **20a–f** can be obtained from tetraacetylglycoluril **11a** [34]. In this reaction, mixed *N*-acetylderivatives of compounds **20d, e, f** can also be obtained in acceptable yields (Scheme 16).

Based on the known properties and methods for the preparation of glycoluril *N*-nitroderivatives, an alternative procedure [9] for the synthesis of *N*-nitroamides and *N*-nitroureanes by nitration of the corresponding *N*-alkylamides and *N*-alkylureas with nitrogen pentoxide in liquid carbon dioxide CO_2 as reaction medium was developed. The nitration procedure [9] was tested using unsubstituted glycoluril **1a** as a model.



Scheme 16. Preparation of a number of *N*-nitroderivatives of glycoluril **20a-f** using tetraacetylglycoluril **11a**

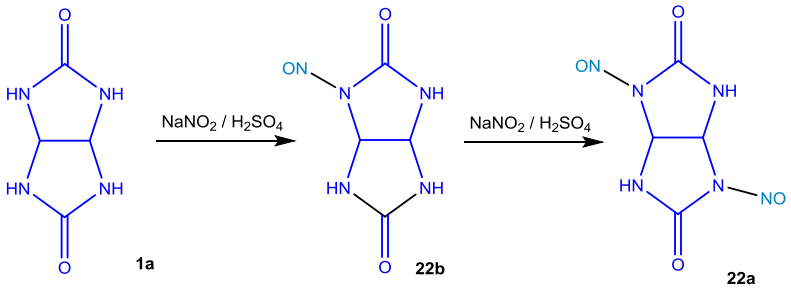
The studied *N*-nitration conditions were also used in the synthesis of mono-, di-, and tetranitro-1,5-disubstituted glycolurils **20a–c, g–s** [71]. It should be noted that the authors [71] failed to obtain or observe the presence of any trinitroderivatives of glycolurils, similar to what was reported by Boileau [5] (Scheme 17).



Scheme 17. Synthesis of mono-, di- and tetranitro derivatives of glycolurils

Thus, *N*-nitration of glycolurils **1a, b, g, h, 21a, b** with 100 % nitric acid leads to the exclusive formation of mononitroderivatives **20c, g–i** with a yield of more than 50 %. When using a solution of mixed acids 100 % HNO_3 and 98 % H_2SO_4, dinitroglycolurils **20a, j–m** are formed. And when using more aggressive conditions (a mixture of trifluoroacetic anhydride and 100 % HNO_3) tetranitroderivatives of glycolurils **20b, n–p** can be obtained (Scheme 17).

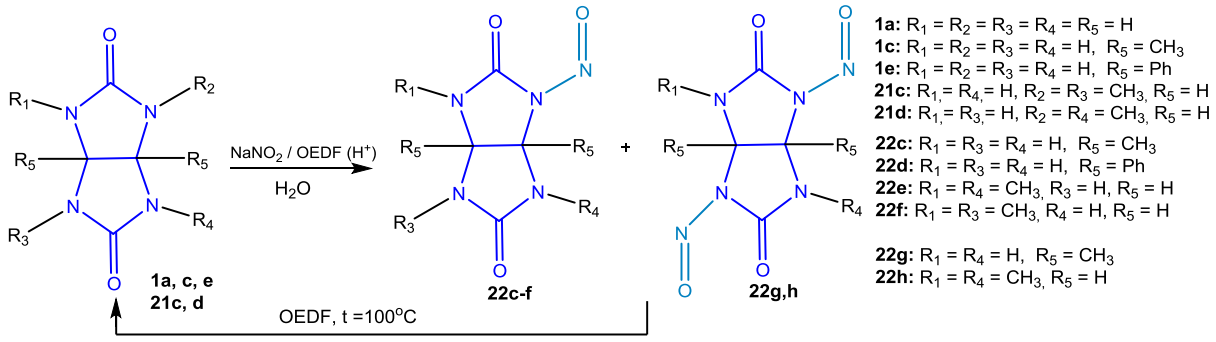
As a pore-forming agent in the synthesis of thermoplastic polymers, 2,6-dinitroso-2,4,6,8-tetraazabicyclo[3.3.0.]octane-3,7-dione (dinitrosoglycoluril) **22a** is known [40, 72], which is obtained by *N*-nitrosation of glycoluril **1a** with sodium nitrite in the presence of a mineral acid. This reaction is accompanied by the formation of the intermediate mononitrosoglycoluril **22b** (Scheme 18).



Scheme 18. *N*-nitrosation of glycoluril **1a** [41]

Mononitrosoglycoluril **22b** is always synthesized *in situ* at the first stage of nitrosation of glycoluril **1a** with alkali metal nitrites and nitric acid. A targeted isolation of mononitrosoglycoluril **22b** was carried out for further *N*-hydroxymethylation reactions [41].

In work [72], a number of *N*-nitrosoderivatives of glycoluril **22a–h** were synthesized using sodium nitrite and 1-hydroxyethylidene diphosphonic acid (HEDP) as a "green" catalyst (Scheme 19).



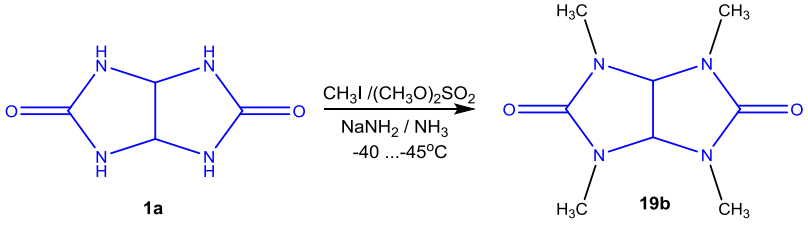
Scheme 19. The synthesis of *N*-nitrosoderivatives of glycoluril [72]

It was found [72] that when using ratios of 1 part of substrate to 2 parts of HEDP, predominantly *N*-mononitrose-substituted glycolurils **22a–f** were formed. Nitrosoglycolurils **22a–h** were isolated in 10–70 % yields. The relatively low yield of mononitrosodiphenylglycoluril **22d** was due to the low water solubility of the initial substrate **1e**.

In most cases, *N*-nitrosoderivatives are unstable and at high temperatures (100 °C) their decomposition rate increases (especially at low pH). The authors of [72] found that substances **22a–h**, when heated with 1 equivalent of HEDP, hydrolyze to the starting glycolurils **1a, c, e, 21c, d** with the destruction of the N–N bond.

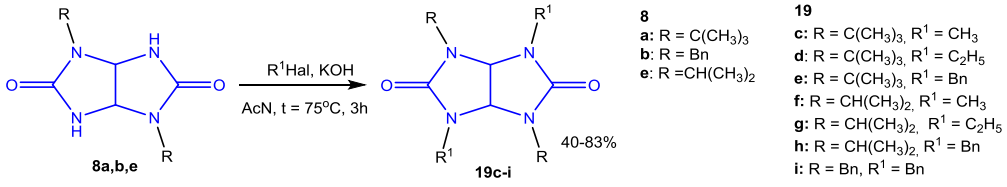
6 Alkylation of glycolurils and the Mannich reaction

It is known [1, 2] that *N*-alkylsubstituted derivatives of glycoluril are pharmacologically active, which leads to a wide interest in these compounds and methods for their synthesis. However, *N*-alkylglycolurils are mainly obtained by condensation of dialkylureas **3** with 1,2-dicarbonyl compounds **2**. Direct alkylation processes at nitrogen atoms are only presented using dimethyl sulfate [73] and methyl iodide [74, 75] to obtain 2,4,6,8-tetramethyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (tetramethylglycoluril) **19b** (Scheme 20). Usually *N*-alkylation reactions of glycoluril **1a** are carried out in liquid ammonia at low temperatures [73–75].



Scheme 20. *N*-Alkylation of glycoluril **1a** in the synthesis of tetramethylglycoluril **19b**

A new method for obtaining tetraalkylsubstituted glycolurils **19c–i** under milder conditions was found [76, 77]. This method describes the treatment of *N*-dialkylglycolurils **8a, b, e** with alkylating agents, namely CH_3I, C_2H_5Br, $C_6H_5CH_2Cl$, in acetonitrile in the presence of KOH base (Scheme 21).



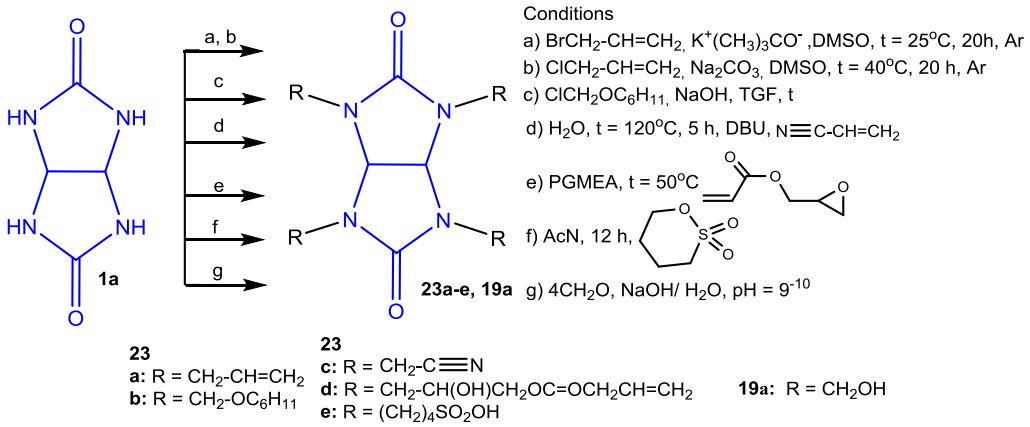
Scheme 21. Reaction of *N*-dialkylglycolurils **8a, b, e** with alkylating agents

Initially, the optimal conditions for the synthesis of dibenzyl-*ditert*-butylglycoluril **19h** with a yield of 83 % were studied. The reaction conditions under which optimal yields of tetraalkylglycolurils **19c–i** were achieved were as follows: duration 3 hours, reaction temperature 75 ºC, molar ratio 1: 4 of disubstituted glycoluril **8** to alkyl chloride, respectively. Thus, *N*-alkylation reaction of dibenzylglycoluril **8b** to obtain tetrabenzylglycoluril **19i** in 63 % yield by treating the compound with benzyl chloride in acetonitrile was successfully carried out (Scheme 21) [77].

The use of acetonitrile as a solvent contributed to obtaining better product yields, while DMSO and DMF solvents did not contribute to satisfactory yields of tetraalkylglycolurils **19c–i** [77]. The authors [77] found that benzyl chloride is the most suitable alkylating agent in the synthesis of product **19i**, in comparison with benzyl bromide. It was also shown that the *N*-alkylation reaction of 2,6-dibenzylglycoluril **8b** is currently the only way to obtain tetrabenzylglycoluril **19i**.

N-Alkylated and *N*-allylated derivatives of glycoluril are widely used [78–83].

Substance **23a** was obtained by *N*-allylation of glycoluril **1a** with allyl bromide in the presence of potassium *tert*-butoxide or with allyl chloride in the presence of sodium carbonate [78] according to Scheme 22.



Scheme 22. Synthesis of glycolurils **23a-e**, **19a** and reaction conditions

Antireflective coating compositions for photoresistors containing a crosslinking component, tetracyclohexamethoxyglycoluril **23b,** were studied [79]. Tetrasubstitutedglycoluril **23b** was synthesized by N-alkylation of **1a** with chloromethoxycyclohexane (Scheme 22).

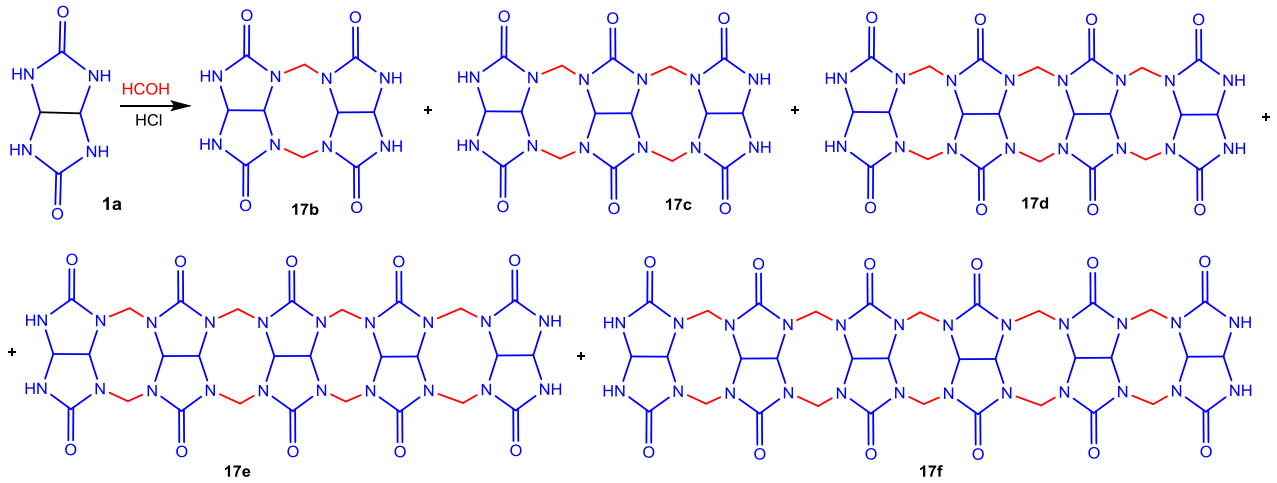
The synthesis of tetra(2-cyanoethyl)glycoluril **23c** with a yield of 61 % was carried out by the reaction of acrylonitrile with glycoluril **1a** in an aqueous medium in the presence of diazabicycloundecene as a base [80] (Scheme 22).

It was shown that glycoluril **1a** reacted with glycidylacrylate in 1-methoxy-2-propanol acetate at 50 °C to form tetrasubstituted glycoluril **23d** (Scheme 22) [81].

Based on bisurea **1a**, a new sulfonic derivative — tetrakis(butane-1-sulfonic acid)glycoluril **23e** was obtained in 95 % yield (Scheme 22). Substance **23e** was used as an effective catalyst for the synthesis of new spiropyrans in boiling water [82].

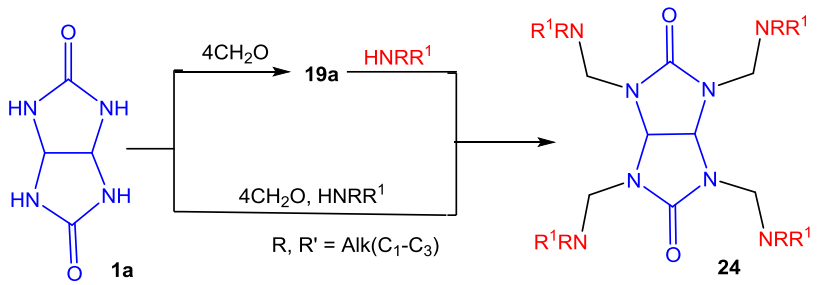
Thus, among *N*-hydroxyalkylglycolurils, 2,4,6,8-tetrahydroxymethyl-2,4,6,8-tetraazabicyclo[3,3,0]-octane-3,7-dione (tetrahydroxymethylglycoluril) **19a** has the greatest synthetic value. Substance **19a** was synthesized by a typical *N*-formylation reaction of glycoluril **1a** in an alkaline medium (Scheme 22) [83]. Tetrahydroxymethylglycoluril **19a** is currently widely used as a cross-linking agent in the production of glycoluril-formaldehyde resins, high-quality thermoset coatings; in the synthesis of supramolecular objects, as well as a bactericidal agent for aqueous compositions [84, 85].

In the reactions of glycoluril **1a** with formaldehyde, by changing the ratio of initial reagents, it is possible to obtain dimers **17b** and other oligomeric molecules **17c-f** [86] (Scheme 23).



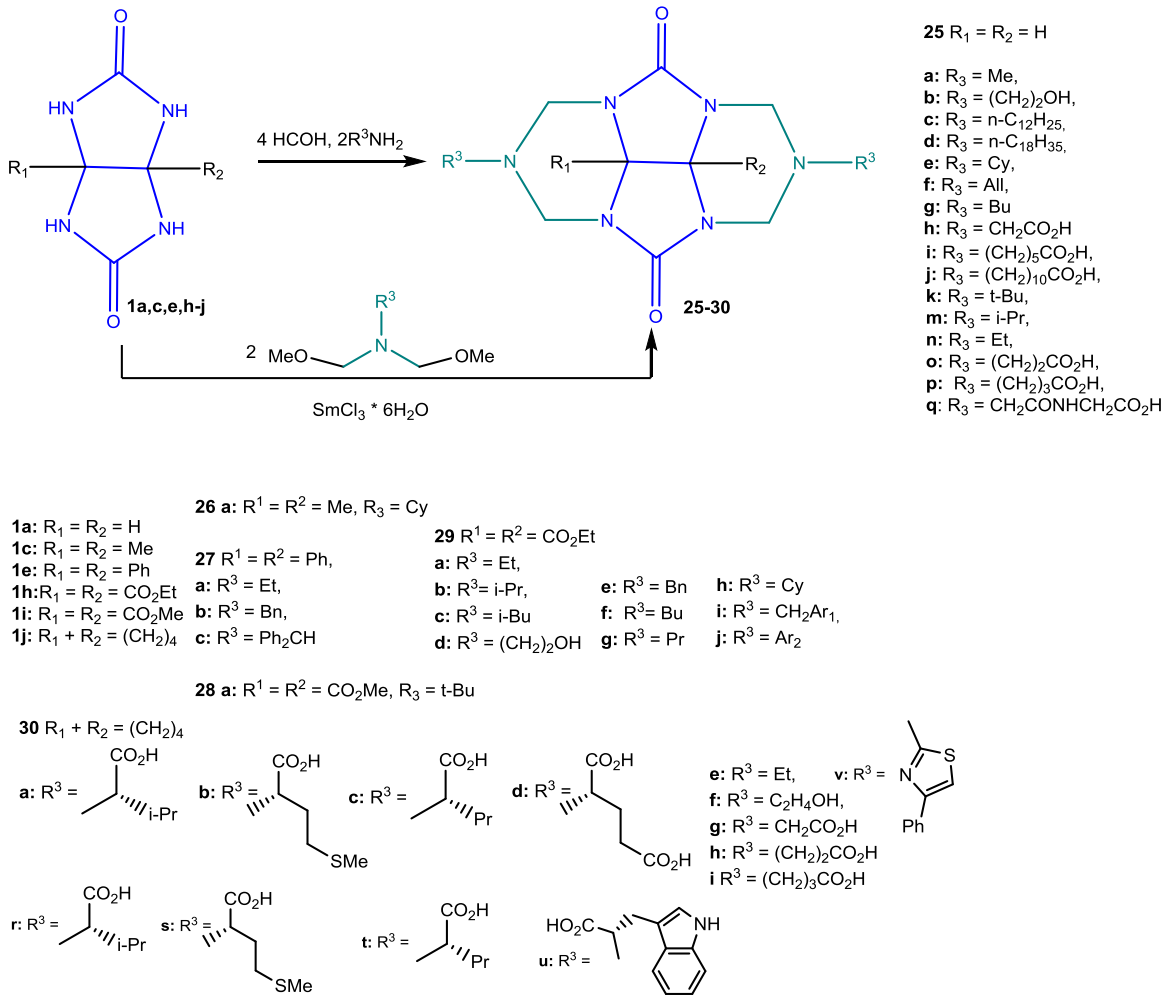
Scheme 23. Synthesis of macrocyclic derivatives of glycoluril [86]

A number of *N*-tetraaminomethylated derivatives of glycoluril **24** was obtained by the Mannich reaction, or stepwise through the intermediate tetrahydroxymethylglycoluril **19a** [41] (Scheme 24). Aminomethylated glycolurils **24** at high pH undergo decomposition at the N–CH_2 bond with the formation of the initial glycoluril **1a** [41].



Scheme 24. The synthesis of *N*-tetraaminomethylated derivatives of glycoluril by the Mannich reaction

The reaction of glycoluril **1a** with formaldehyde became the basis for rapid progress in the chemistry of fused polycyclic glycolurils — cucurbit[n]urils, bambus[n]urils and other objects of supramolecular chemistry [86, 87]. For the synthesis of tetracyclic derivatives of glycoluril **25–30** (Scheme 25), three-component condensation of glycolurils **1a, c, e, h–j** with formaldehyde and amines was carried out [87, 88].



Scheme 25. The synthesis of tetracyclic derivatives **25–30** by three-component condensation of glycolurils with formaldehyde and amines [87]

Also, the three-component condensation approach was used in the synthesis of three tetracyclic compounds **25a, b, v** by the interaction of glycoluril **1a** with formaldehyde (4 mol) and 2 mol of the corresponding amine (methylamine, 2-(hydroxyethyl)amine or 4-phenylthiazol-2-amine) (Scheme 25) [87, 88]. Tetracyclic compound **25a** was synthesized in 33 % yield and substance **25b** in 80 % yield and the yield of compound **25v** was 17 % [88].

A new method for the synthesis of compounds **25b, e, l, m** based on the condensation of glycoluril **1a** with *N*,*N*-bis(methoxymethyl)alkylamines (R^3 = Cy, 2-Pr, t-Bu, $(CH_2)_2OH$) in a $CHCl_3$–EtOH medium and using $SmCl_3$*$6H_2O$ as a catalyst was proposed (Scheme 25) [87]. The target compounds **25b, e, l, m** were isolated by column chromatography, where the yields of **25b, e, l, m** were 70–81 %. Compound **26a** was obtained by the reaction of 1,5-dimethylglycoluril **1c** with a 30 % solution of formaldehyde and cyclohexylamine at reflux in isobutanol. Compound **27a** (in 12 % yield) was condensed using 1,5-diphenylglycoluril **1e**, formaldehyde, and ethylamine by refluxing the starting materials in MeOH solution. Compounds **27b**, **c** were also synthesized in 90 % yield in acetonitrile at room temperature. Dicarboxylate **28a** (90 % yield) was synthesized by the condensation reaction of dimethyl-2,5-dioxoglycoluril-3a,6a-dicarboxylate **1i**, paraformaldehyde, and *tert*-butylamine in acetonitrile at room temperature.

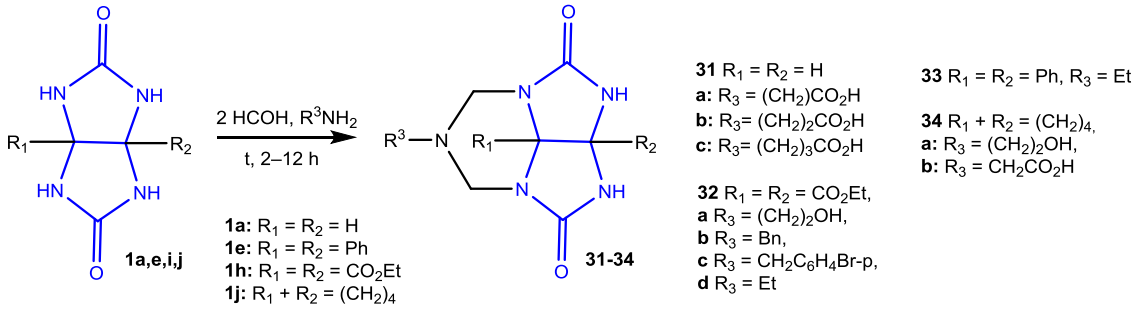
Three-component condensation was used mainly to obtain diethyl-2,6-dialkyl-4,8-hexaazacyclopenta[def]fluorene-3a-1,4-dicarboxylates **29a–j** (Scheme 25) by condensation of diethyl-2,5-dioxoglycoluril-3a, 6a-dicarboxylate **1h** with formaldehyde and alkyl-, aryl- or alkylarylamines [87].

In the process of synthesizing compounds **30a–i**, solutions of the corresponding amines in MeOH or MeCN were added dropwise to a mixture of glycoluril **1a** with formaldehyde. The yields of tetracyclic compounds obtained by this method varied from 10 to 76 %. To increase the yield of tetracyclic com-

pounds **30b–e** (up to 90 %), acetonitrile was used as a solvent for amines, and the reaction mixture was stirred for 12 h at room temperature [87].

The synthesis of tetracycles **30j** was carried out in various solvents. The optimal conditions found for the reactions of diethoxycarbonylglycoluril **1h** with formaldehyde and aromatic amines (aniline, *p*-toluidine, *m*-toluidine, *p*-methoxyaniline, *p*-isopropylaniline, *p*-chloroaniline, *p*-bromoaniline, *p*-iodaniline, *p*-ethynylaniline) were: dimethylformamide as a solvent and keeping the reaction mixture at 120 °C for 16 h, where the yields of products **30j** were 24–61 % (Scheme 25) [87].

Synthesis of tricyclic derivatives of glycoluril, 2a,2a[1]-disubstituted 6-alkyltetrahydro-pentaaza-cyclopenta[cd]inden-1,4-diones **31-34** was carried out by three-component condensation of glycolurils **1a, e, h, j** with formaldehyde and amines or potassium of amino acid salts (in the form of solutions in an appropriate solvent) (Scheme 26) [86].

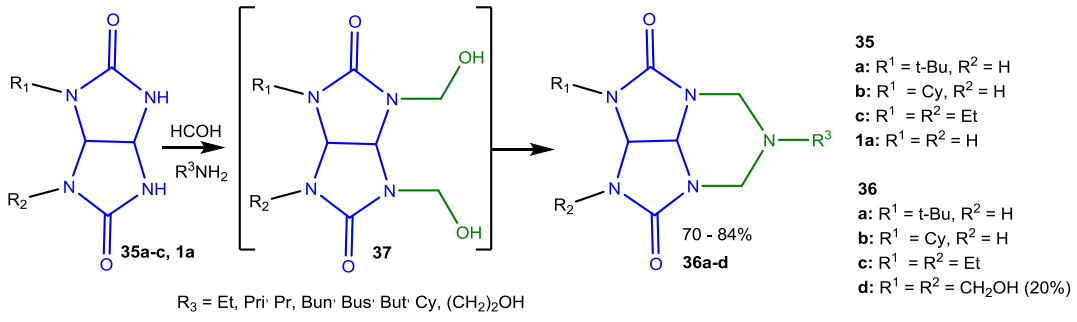


Scheme 26. The synthesis of tricyclic derivatives of glycoluril **31-34** [87]

The reactions shown in Scheme 26 were carried out in solutions of H_2O, MeOH, EtOH and MeCN. Tricyclic compounds **31a** c were obtained in 20–50 % yield by keeping the reaction mixtures at 90 °C for 2 hours. The observed products were formed by oligomerization between *N*-(hydroxymethyl)glycolurils having different degrees of hydroxymethylation at nitrogen atoms, as well as by oligomerization of these compounds with amino acids [89]. Synthesis of compound **31a** (yield 20 %) was carried out in acetonitrile, and compound **32b** in methanol. Compounds **32d** and **33** were prepared in a similar manner using EtOH instead of MeOH. The yields of products **32b–d**, **31** were 45–80 %. (Scheme 26) [87].

Tetracyclic compounds **34a, b** were isolated as side products in the reactions of compound **1j** with (2-hydroxyethyl)amine and *N*-carbamoylglycine (in the form of potassium salt) (Scheme 26) under conditions similar to those used for the synthesis of pentacyclic products **31** (H_2O, pH 9, 90 °C, 2 hours) [90].

A condensation reaction of 1-(*tert-butyl*) or 1-*cyclohexyl*glycolurils **35a, b** with formaldehyde and aliphatic amines was carried out (Scheme 27), and a result of the reaction, 2-substituted-6-alkyltetrahydro-pentaazacyclopenta[cd]inden-1,4-diones **36a–c** were obtained in high yields from 70 to 84 % (14 examples) through the formation of intermediate compounds **37** [90].

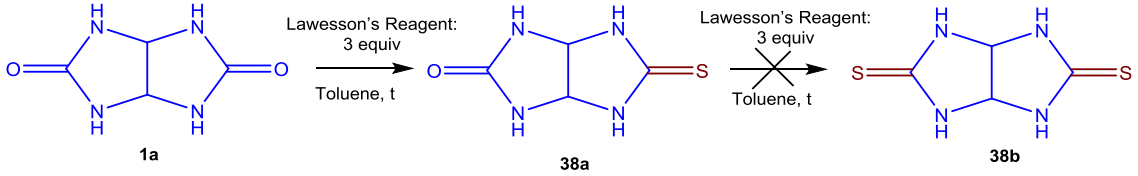


Scheme 27. The synthesis of tricyclic derivatives of glycoluril **36a–d** [87]

Condensation between glycoluril **1a**, formaldehyde and isopropylamine in acetonitrile at room temperature led to the synthesis of 2,3-bis(hydroxymethyl)-6-isopropylhexahydro-1H-2,3,4a,6,7a-pentaazacyclopenta[cd]-indene-1,4(2H)-dione **36d** in 20 % yield (Scheme 27) [87].

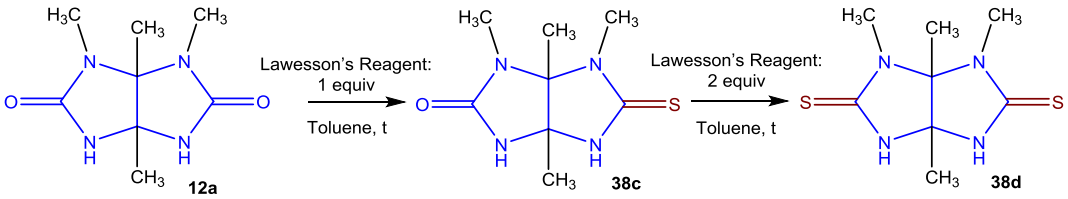
7 Thioderivatives of glycoluril

Mono-, and dithioglycolurils, as found in [48], can be obtained by the action of Lawesson's reagent on glycolurils. Preliminary studies of glycoluril **1a** transformations to the corresponding dithioderivative **38b** were unsuccessful, however, monothioglycoluril **38a** using Lawesson's reagent was obtained (Scheme 28).



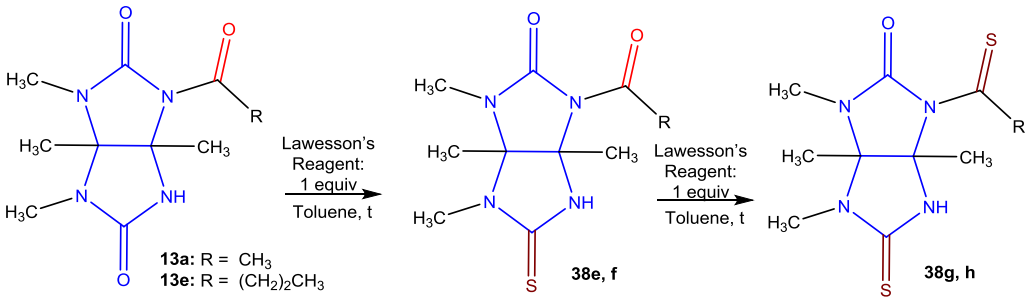
Scheme 28. The synthesis of monothioglycoluril **38a**

Heating 1,2,5,8-tetramethylglycoluryl **12a** with 1 equivalent of Lawesson's reagent readily formed thioglycoluryl **38c**, and increasing the amount of reagent to 3 equivalents led to the corresponding dithioyl derivative **38d** (Scheme 29).



Scheme 29. Thionization of tetramethylglycoluril **12a**

Treatment of monoacylglycolurils **13a, e** with Lawesson's reagent results in highly selective monothionization of the glycoluril system with the formation of individual products **38e** or **38f**, respectively. Substitution of oxygen by sulfur occurs at 60 °C in the carbonyl group of glycoluril **13a, e**, which is the furthest away from the acylgroup of the substituent (Scheme 30).



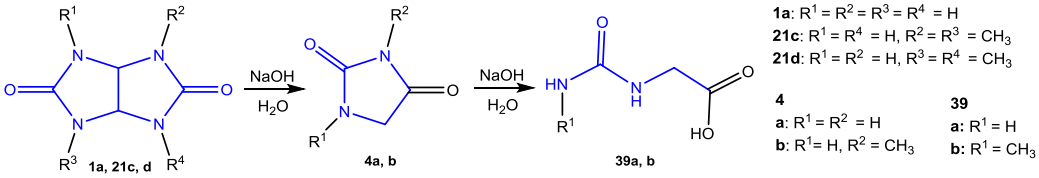
Scheme 30. Treatment of monoacylglycolurils **13a, e** with Lawesson's reagent

Alcoholysis of glycolurils **38e, f** using sodium ethoxide in THF leads to the elimination of the acetyl group, with the formation of a pure sample of glycoluril monothioderivative **38c**. The structures of thioderivatives of glycolurils were studied by X-ray diffraction analysis [48].

8 Hydrolysis of glycolurils

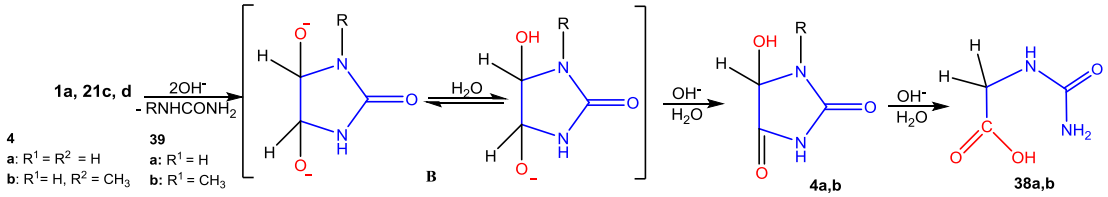
It is known that glycolurils are stable in a strongly acidic environment and do not enter into hydrolysis processes [91]. However, the hydrolytic properties of glycolurils under alkaline conditions are much less studied.

The authors [92] studied the ability of glycoluril **1a** and its dimethylderivatives **21c, d** to hydrolytic decomposition under alkaline conditions. It was shown that the hydrolysis of glycoluril **1a** to hydantoin **4a** at 100 °C in an alkaline medium proceeds rather quickly (10 minutes). A separate hydrolysis reaction of hydantoin **4a** under the action of aqueous NaOH leads to the formation of hydantoic acid **39a**. Dimethylderivatives of glycolurils **21c, d** react similarly (Scheme 31).



Scheme 31. Alkaline hydrolysis of glycoluril **1a** and dimethylglycoluril **21c, d** [92]

It is possible that glycolurils **21c, d** under the action of alkali at the initial stage through the elimination of the corresponding ureas form type B anions which undergo rearrangement to hydantoins **4a, b**, and the latter are easily hydrolyzed to hydantoic acids **39 a, b** (Scheme 32).

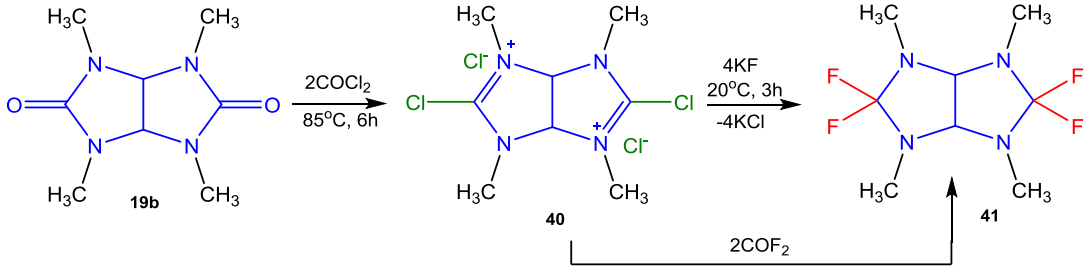


Scheme 32. Rearrangement of glycolurils **1a, 21c, d** to hydantoins **4a, b** under alkaline conditions [92]

9 Reactions on the carbonyl group of glycolurils

Reactions on the carbonyl oxygen of glycolurils in the literature are presented only by the reactions of *O*-reduction and *O*-alkylation. It is known that tetramethylglycoluril **19b** has high reaction stability to various reagents [91], and the replacement of carbonyl oxygen with a chlorine atom can sharply increase the reactivity of the latter.

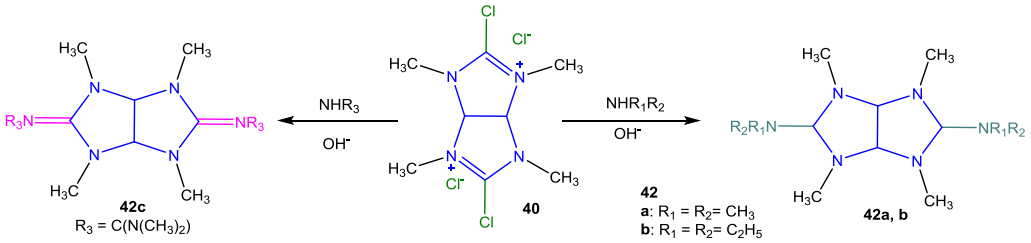
The authors [93] studied the reaction between oxolyl chloride and tetramethylglycoluril **19b**, which resulted in the formation of salt **40** with a reduced carbonyl group containing chlorine atoms. The reaction was carried out in an inert atmosphere at a temperature of 80–90 °C for 6 hours (Scheme 33).



Scheme 33. The synthesis of halogen derivatives of tetramethylglycoluril **19b**

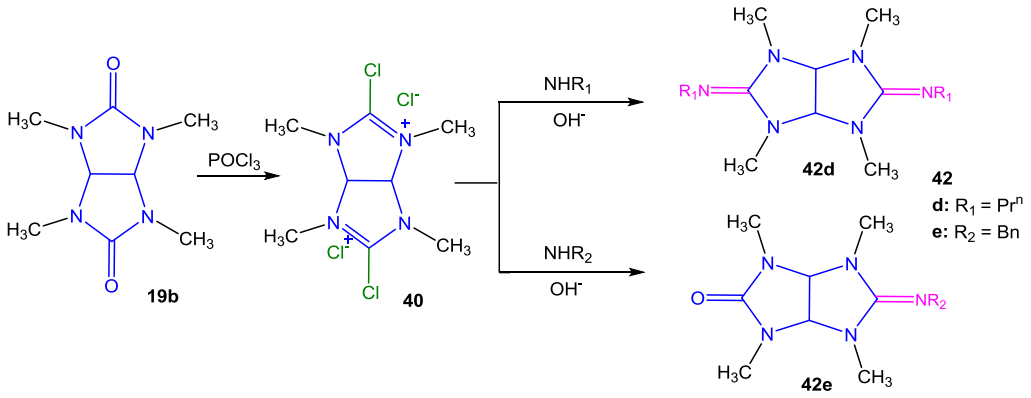
In order to obtain fluorinederivatives of glycolurils, the interaction of the chlorine salt of tetramethylglycoluril **40** with potassium fluoride in anhydrous acetonitrile was studied, as a result of which tetramethyltetrafluoroglycoluril **41** was obtained (Scheme 33). An alternative method for the preparation of tetramethyltetrafluoroglycoluril **41** is the reaction of glycoluril **40** with COF_2.

The authors [93] additionally carried out the functionalization of the chlorine-containing salt of tetramethylglycoluril **40** with amines of various structures: tetramethylguanidine, dimethyl- and diethylamine. Reactions were carried out at room temperature in anhydrous methylene chloride, where crystalline compounds **41a** c with potential biological activity were obtained (Scheme 34).



Scheme 34. The functionalization of the chlorine-containing salt of tetramethylglycoluril **39** with amines

Tetramethyltetrachloroglycoluril **40** was also obtained by the action of phosphorus oxychloride on tetramethylglycoluril **19b**. The reaction product of salt **40** with propylamine in the "One-pot" synthesis was N,N'-di(*N*-propylamino)-2,4,6,8-tetramethyl-2,4,6,8-tetraazabicyclo[3.3.0.]-octane-3,7-diylidene **42d** (Scheme 35) [57].



Scheme 35. The "One-pot" functionalization of the chlorine-containing salt of tetramethylglycoluril **40**

The addition of benzylamine at the second stage of the "One-pot" reaction (*in situ*) led to the formation of monosubstituted glycoluril **42e** (Scheme 35) as the main product, which can be explained by steric hindrances associated with the bulk of the benzylamine molecule and the spatial configuration of the starting compound.

Conclusion

In the present work, the main physico-chemical and spectral characteristics of glycoluril as the main representative of bicyclic bisureas were presented and discussed. The chemical properties of glycoluril and its derivatives currently known in the literature and the ways of their modification were also discussed. The review demonstrated the reactions of *N*-halogenation, *N*-acylation of glycolurils; obtaining phosphorus-, nitro- and nitroso derivatives of glycolurils; *N*-alkylation, Mannich reactions, thionization, hydrolysis and reactions at the carbonyl group of glycolurils. Methods for the preparation of macrocyclic compounds based on glycoluril were considered.

The variety of glycoluril derivatives is due to various substituents in the bicyclic structure, which directly affect the properties of the glycoluril skeleton. And the influence of substituents on the geometry and on the NMR chemical shifts of the bicyclic skeleton of glycoluril was considered in the works [33, 35].

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Information about authors*

Ponomarenko, Oksana Vladimirovna (corresponding author) — PhD, Chemistry and Biotechnology Department, Sh. Ualikhanov Kokshetau University, Abai st., 76 020000, Kokshetau, Kazakhstan, e-mail: oksana.ponomarenko.88@mail.ru; https://orcid.org/0000-0002-8172-5139

Panshina, Svetlana Yur'evna — PhD, Organic Chemistry and Polymers Department, Karagandy University of the name of academician E.A. Buketov, Universitetskaya st., 28, 100024, Karaganda, Kazakhstan; e-mail: janim_svetatusik@mail.ru; https://orcid.org/0000-0001-6824-2645

Bakibaev, Abdigali Abdimanapovich — Doctor of Chemical Sciences, Professor, Leading Researcher of the Laboratory of Organic Synthesis, National Research Tomsk State University, Lenin st., 36, 634050, Tomsk, Russia; e-mail: bakibaev@mail.ru; https://orcid.org/0000-0002-3335-3166

Erkasov, Rahmetulla Sharapidenovich — Doctor of Chemical Sciences, Professor, Department of Chemistry, L.N. Gumilyov Eurasian National University, Satpayev Str., 2, 010000, Astana, Kazakhstan, e-mail: erkass@mail.ru; https://orcid.org/0000-0001-5148-8147

Kenzhebaj, Madina Sayatkyzy — 3th year Student of Chemistry Specialty, Department of Chemistry and Biotechnology, Sh. Ualikhanov Kokshetau University, Abai st., 76, 020000, Kokshetau, Kazakhstan, e-mail: madinakenzhebaj@gmail.com

Montaeva, Anel' Sabyrgel'dievna — 3th year Student of Chemistry Specialty, Department of Chemistry and Biotechnology, Sh. Ualikhanov Kokshetau University, Abai st., 76, 020000, Kokshetau, Kazakhstan, e-mail: montaeva200@gmail.com

*The author's name is presented in the order: *Last Name, First and Middle Names*