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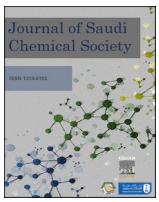

Review

Methods of synthesizing glycoluril-based macrocyclic compounds as precursors for polymeric compounds

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ABSTRACT

This review study considers the classification of data on synthesis methods and practically valuable features of glycoluril-based macrocyclic nitrogen-containing compounds as precursors for polymeric compounds. General data about glycoluril and tetra-*N*-hydroxymethylglycoluril as parental bases for various macrocyclic compounds were considered. Generalized experimental facts about methods for glycoluril direct *N*-functionalization and its *N*-hydroxymethyl derivative reactions in macrocycles and polymeric compound synthesis are given.

1. Introduction

Currently, glycoluril is used for producing pharmaceuticals [1], explosives [2–5], linking agents, special purpose polymers [6] and other valuable compounds.

In recent decades, a new field in glycoluril chemistry that has been actively developing is the creation of macrocyclic compounds with unique controlled properties based on glycoluril and its derivatives - (cucurbit[n]urils, bambus[n]urils, tiara[n]urils, «molecular clips» and the formation of supramolecular systems involving them. Supramolecular compounds obtained using glycoluril have been studied as components of organic semiconductor materials [7], auxiliary compounds for pharmaceuticals, such as prolongators and controlled release molecular containers [8–10], materials with "molecular recognition" properties and molecular sensors for express analysis of amphiphilic components, such as surface-active substances, bacterial endotoxins and biogenic amines [11–15], which use glycoluril **1** as a construction material.

Definite success in researching cucurbit[n]uril and bambus[n]uril properties and synthesis methods is a subject for freestanding generalizations [16–23].

There are a number of generally acceptable methods of glycoluril synthesis [24–26], of which methods based on carbamide reactions with 1,2-dicarbonyl compounds are of practical interest. This synthetic approach allowed us to obtain various glycolurils unsubstituted along nitrogen atoms, glycolurils with cyclic fragments at C(3a)-C(6a) atoms, 1-substituted glycolurils, 1,3,4-trisubstituted glycolurils, and 1,4-di-, 1,6-di-, and 1,3,4,6-tetrasubstituted glycolurils. Another way to prepare glycolurils is using 4,5-dihydroxyimidazolidine-2-one (DHI) intermediates as synthons, followed by glycoluril formation.

A synthetic variety of glycolurils is reached by changing substituents in standard reactions of *N*-alkylation, *N*-acylation, *N*-halogenation, *N*-nitration, *N*-nitrosation, *N*-hydroxyalkylation, etc. [27,28].

Given that the trajectories of glycoluril formation are not exhaustive methods of its synthesis, the success achieved in modifying these methods is defined by the selection of new catalysts and conditions

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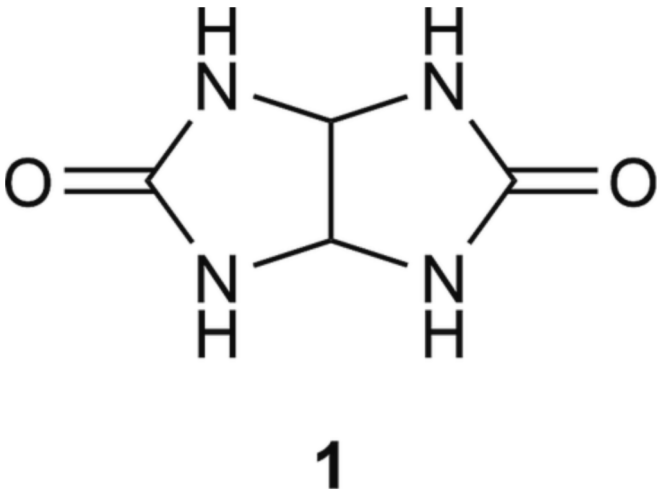

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Fig. 1.1. Glycoluril molecule.

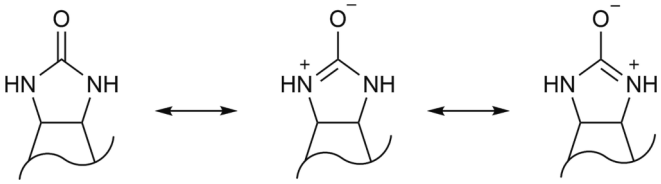


Fig. 1.2. Reaction centers in glycoluril.

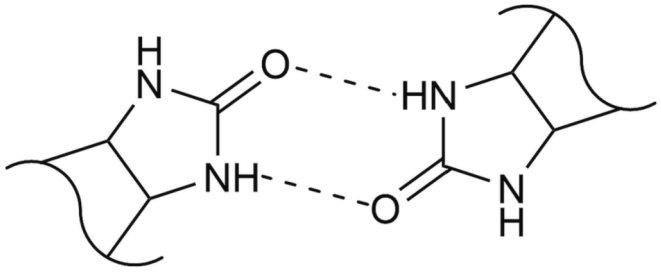


Fig. 1.3. Hydrogen bonds in crystalline glycoluril.

Table 1
Physicochemical properties of glycoluril **1**.

Parameter	Data
Melting point, °C	360(decomposes)
Solubility	Insoluble in most solvents Slightly soluble in DMF, DMSO, acetic anhydride, H_2O
IR-spectrum, cm^{-1}	3209 (NH); 1675 (C = O)
^1H NMR (DMSO-d_6)	5.24 (2H, CH)7.16 (4H, NH)
^{13}C NMR (DMSO-d_6)	160.3 (C = O)64.6 (CH)

allowing the combination of simplicity of the process and efficiency increase [29–32].

The aim of this review is to raise awareness of interesting and practically useful synthesis methods and properties of glycoluril-based macrocyclic nitrogen-containing compounds as precursors for polymeric compounds and to encourage new research in this promising field.

Separate parts of this generalized research on glycoluril-based polycyclic heterocycles are given in studies [33,34].

2. General information about glycoluril

Bicyclic carbamides play an important role in heterocyclic compound chemistry, specifically 2,4,6,8–tetraazabicyclo[3.3.0.]octan-3,7-dione (glycoluril **1**, tetrahydroimidazo[4,5-d]imidazol-2,5(1*H*, 3*H*)-dione) and its compounds (Fig. 1.1). Glycoluril chemistry originated in the second half of the 19th century, when a number of researchers managed to synthesize the original **1**, and it was considered to have a bicyclic structure similar to carbamide [35,36].

However, relatively recently, it was found [37] that the molecule of glycoluril **1a** is not flat and has a 124.1° angle between two imidazolidinone fragments, and nitrogen atoms are located equidistantly from each other. Hydrogen atoms at the methine carbon are *cis*-oriented, and imidazolidinone cycles are characterized as almost flat but having a minor C = O group deviation from the general plane.

Glycoluril **1** is a polyfunctional compound in which the carbamide fragment (Fig. 1.2) defines the properties of the **1** molecule, which are caused by the presence of two reaction centers (4 (–NH) donor groups and 2 (C = O) acceptor groups).

Compound **1** has the form of white crystals with a developed system of strong intermolecular hydrogen bonds (Fig. 1.3), which define the high melting temperature (360 °C – with decomposition) and low solubility of glycoluril **1**.

A more detailed view of glycoluril structure peculiarities is given in the study [38], which says that glycoluril **1** exists in two polymorphic forms that can crystallize in water simultaneously. The polymorphism effect of glycoluril **1** has a significant influence on its physical–chemical properties, and in the case of reactive ability estimation, this effect is neutralized in solutions due to the equal solvent influence on crystalline structure of **1**.

The physical–chemical properties of glycoluril **1** are given in Table 1.

Thus, considering the specific limited solubility of glycoluril **1** (Table 1), usual solvents DMSO-d_6 and D_2O are used most often for identification via the NMR method.

There are some difficulties in identifying glycoluril **1** as well as other NH-group-containing compounds in D_2O, as the chemical shift of NH groups is often hidden due to deuterium exchange. The **1** molecule is defined more clearly in the ^1H NMR spectra in DMSO-d_6, where there are 2 chemical shifts in the 5.24 ppm and 7.16 ppm areas, which correspond to protons of CH and NH groups. In the ^{13}C NMR (DMSO-d_6) spectrum, CH-carbons are revealed at 64.6 ppm, and carbonyl carbons (C = O) resonate at 160.3 ppm [39]. The equivalence of carbon and hydrogen atoms in the bicyclic structure definitely suggests glycoluril space symmetry.

Glycoluril **1** is an active *N*-nucleophile and significantly deactivated p-nucleophile, and the presence of (NH–C = O) bonds with electron-acceptor carbonyl groups makes it a less reactive base. This explains protonation difficulty and tendency toward breakage of products formed in electrophilic attack of nitrogen atom; besides, weak electrophilic properties of carbonyl group are explained by collectivization of two lone pairs of electrons which compensate electron-acceptor effect of carbonyl group. Glycolurils have a tendency to form complexes due to oxygen and nitrogen atoms, which are the most likely coordination centers for complex formation. However, coordination via nitrogen atoms is generally sterically complicated due to its predominantly pyramidal structure; moreover, this center has lower electron density than oxygen.

The most frequently used compounds for making glycoluril metal complexes are *N*-alkylglycolurils, which are potentially polydentate ligands and can perform either monodentate or bidentate-bridge functions with d-metals with binding through C = O groups of carbamide fragments depending on the metal atom's coordination number (Fig. 1.4).

The combination of the abovementioned structural and physical–chemical properties of glycolurils and their polyfunctionality basically define these molecules' ability to form macrocyclic and polymeric

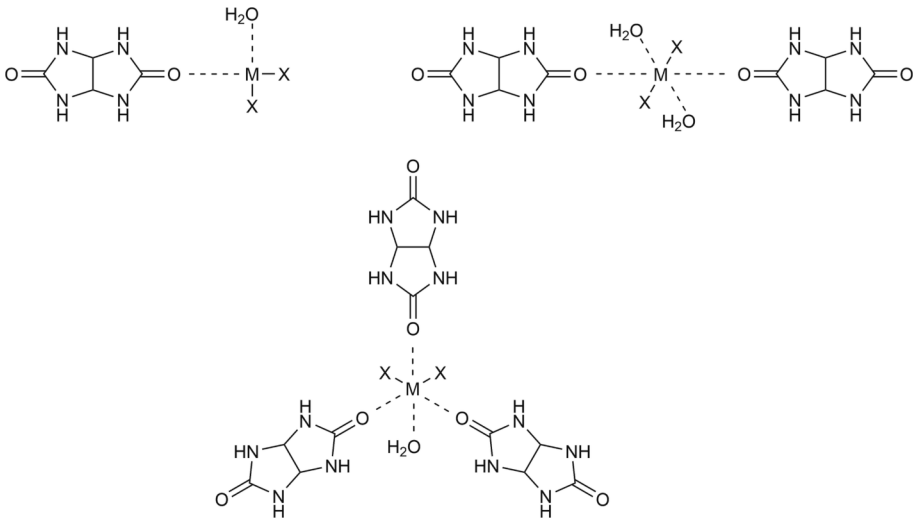


Fig. 1.4. Glycoluril complexes with d-metals.

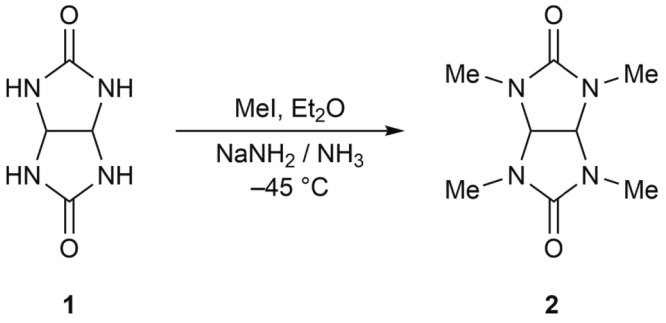


Fig. 2.1. Scheme of glycoluril alkylation.

compounds.

3. Direct *N*-functionalization of glycoluril in macrocycle synthesis

By changing the nature of the substituents during *N*-alkylation of glycoluril **1**, it is possible to regulate the biological activity of its tetra-*N*-substituted compounds [40]. For example, the most frequent methylating agents in tetra-*N*-methylglycoluril synthesis are dimethyl sulfate [41] and methyl iodide [42]; generally, alkylation is performed in liquid ammonia under $NaNH_2$ with alkylhalides (Fig. 2.1).

Although tetra-*N*-methylglycoluril is a highly chemically and biochemically stable compound, a distinctive feature of glycoluril's *N*-alkyl derivatives is the tendency toward complex formation with various metals [43–45], which allows us to expect the possibility of new heteronuclear polycyclic system synthesis.

Studies [46,47] suggest ways of obtaining 2,4,6,8-tetrasubstituted

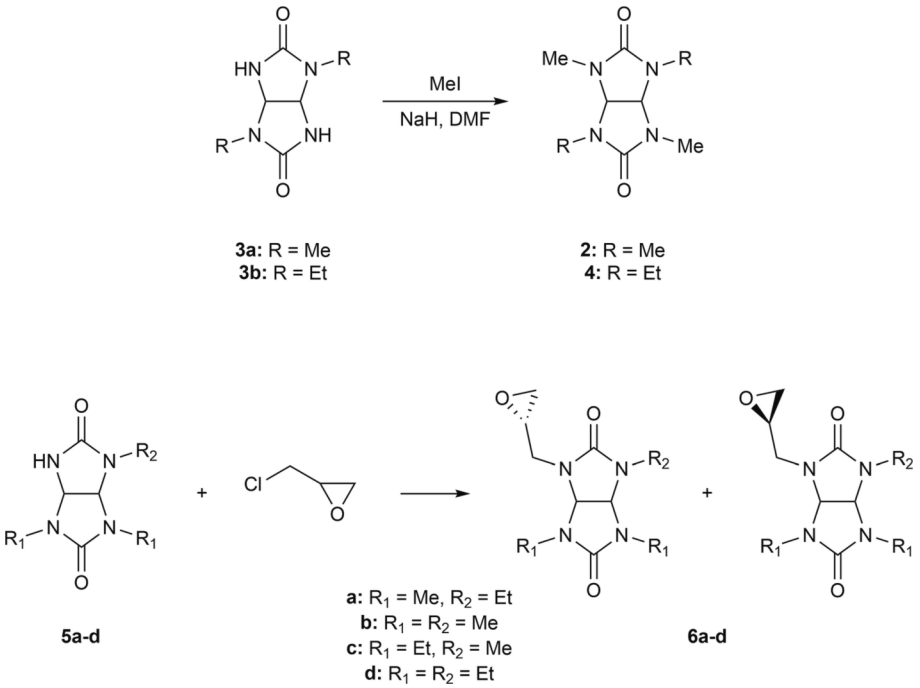


Fig. 2.2. Alkylation of partially substituted glycolurils.

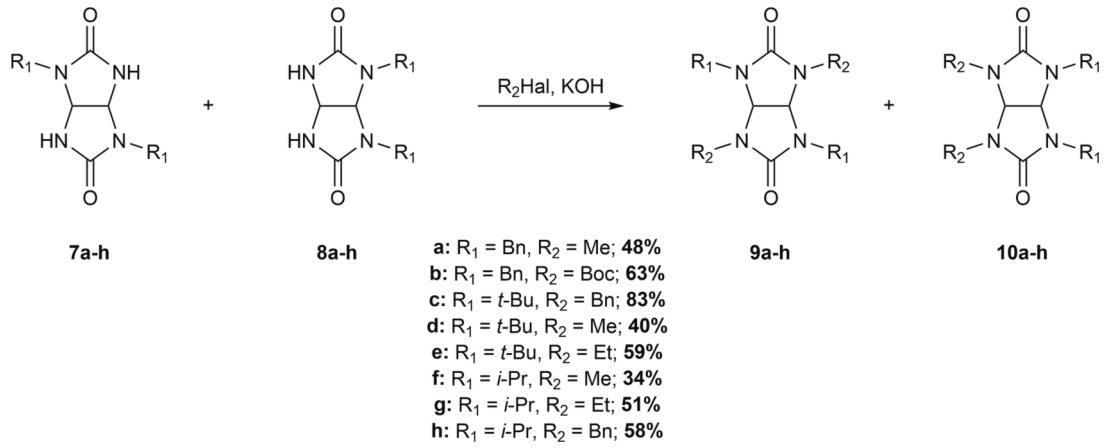


Fig. 2.3. Alkylation of disubstituted glycolurils.

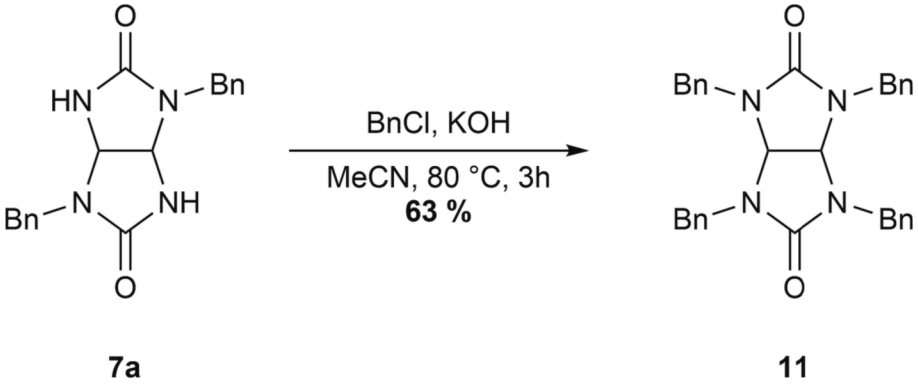


Fig. 2.4. Synthesis of *N,N,N,N*-tetrabenzylglycoluril.

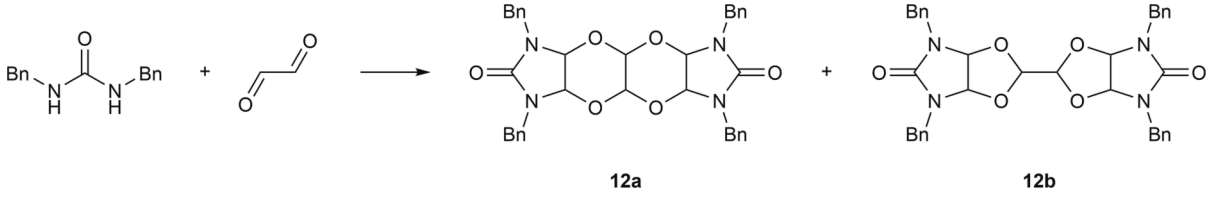


Fig. 2.5. Reaction of dibenzylurea with glyoxal.

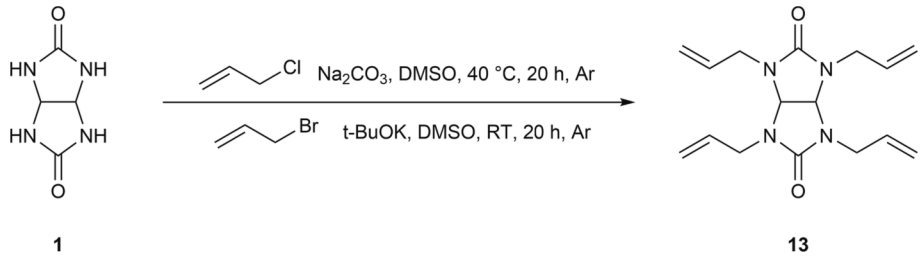


Fig. 2.6. Synthesis of tetraallylglycoluril.

glycolurils through partially substituted glycolurils (Fig. 2.2).

The developed convenient method of tetrasubstituted glycoluril synthesis in an acetonitrile-KOH environment by treating disubstituted glycolurils with alkylating agents (Fig. 2.3) allowed us to expand the line of tetra-*N*-substituted glycolurils not described in the literature before [48]. Initial disubstituted glycolurils were obtained by monosubstituted carbamide cyclization with glyoxal using methods [49] and are a mixture of cis- and *trans*-isomers.

This type of reaction also includes *N*-benzylation of glycoluril **1**, which is interesting due to its use as an effective stabilizer for polymeric materials. Such switching to tetra-*N*-benzylglycoluril **11** was established during *N*-benzylation of 2,6-di-*N*-benzylglycoluril with a target compound yield of 63 % [50] by alkylation with benzyl chloride in acetonitrile (Fig. 2.4). It was concluded that acetonitrile is the most suitable

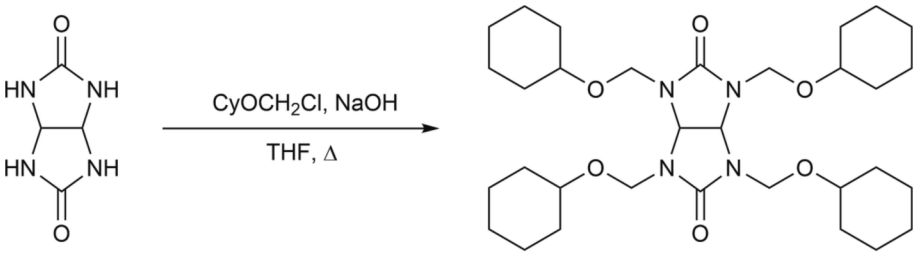


Fig. 2.7. Synthesis of substituted glycoluril that can be used with overcoated photoresist compositions.

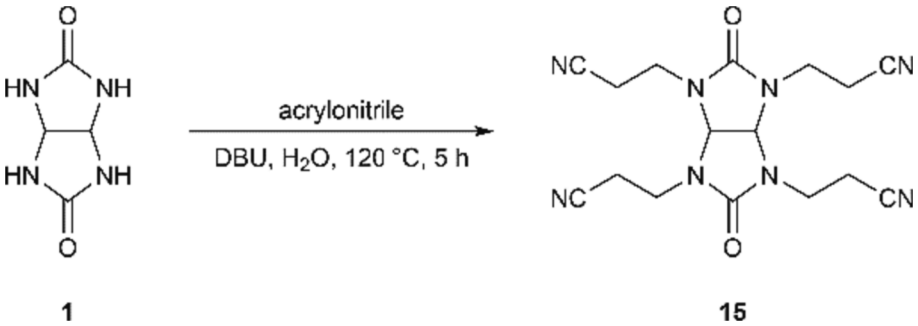


Fig. 2.8. Synthesis of tetra(2-cyanoethyl)glycoluril.

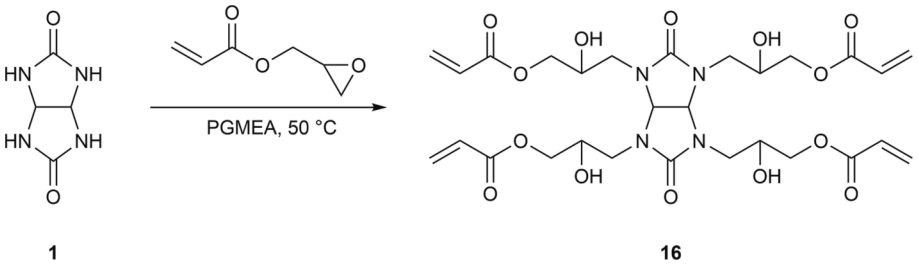


Fig. 2.9. Reaction of glycoluril with glycidylacrylate.

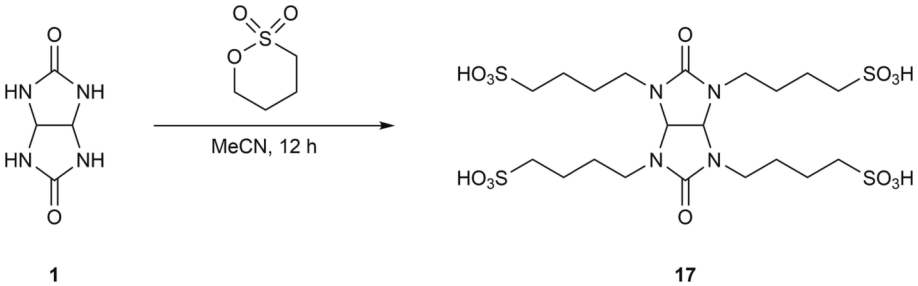


Fig. 2.10. Synthesis of glycoluril tetrakis(butane-1-sulfonic acid).

generic solvent, as its use provided the best experimental results, while DMSO and DMF, similar to direct reaction with glycoluril, did not lead to positive outcomes. It was found that benzyl chloride is better as an alkylating agent, as it provides a higher target product yield than benzyl bromide and is less toxic. This study suggests that the 2,6-dibenzylglycoluril *N*-alkylation reaction is currently the only way of obtaining tetra-*N*-benzylglycoluril.

An alternative way to prepare 2,4,6,8-tetrabenzylglycoluril **11** through condensation of 1,3-dibenzylcarbamide with glyoxal does not provide the desired outcome, as it is accompanied only by the formation of oxo-compounds **12a**–**b**, as shown in Fig. 2.5.

A similar process was previously observed in the study [51] where an analogue of compound **12a**, with the structure of condensed 4 heterocycles was synthesized. An analogue of Compound **12b**, with a bicyclic structure (dioxolane fragment) with methyl substituents, was described in the study [52], with the structure proven by the XRD method.

The importance of *N,N,N,N*-tetraallylglycoluril **13** obtained by allylation of glycoluril **1** with allylchloride in the presence of sodium carbonate (Fig. 2.6) is defined by the fact that it is a convenient precursor for obtaining new polymers due to its polyfunctionality. A new

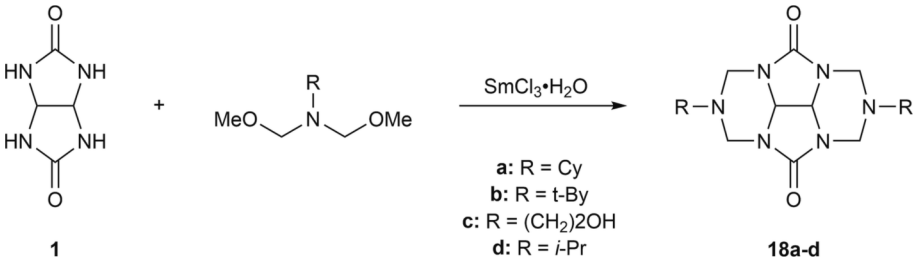


Fig. 2.11. Catalytic cycloamination of glycoluril.

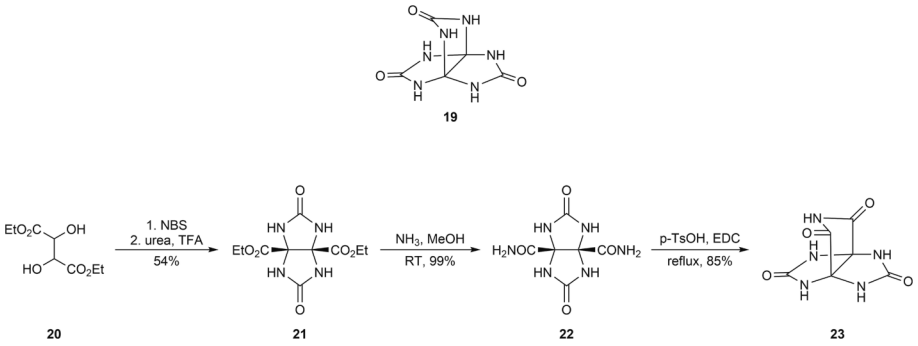


Fig. 2.12. 2,4,6,8,9,11-hexaaza[3.3.3]propellane (**19**) and synthesis of 2,4,6,8,10-pentaaza[3.3.3]propellane (**23**).

Table 2
Conditions of 3,7,9,11-tetraoxo-2,4,6,8,10-pentaaza [3.3.3]propellane nitration.

Nitration mixture	Data
HNO_3/P_2O_5	**21a**, 32 %
HNO_3/CF_3COOH	**21a**, 61 %
HNO_3/Ac_2O	**21a**, 38 %
HNO_3/NO_2BF_4	**21b**, 53 %
NH_4NO_3/CF_3COOH	**21b**, 11 %

functional polymer was obtained by copolymerization of 4-vinylpyridine and *N,N,N,N*-tetraallylglycoluril **13** [53], which was obtained by allylation of glycoluril **1** with allylbromide in the presence of potassium *tert*-butoxide. Tetra-*N*-allylglycoluril **13** was also used to create organosilane polymers [54].

The results given in the patent [55] are of practical interest, where light-reflecting coating compounds were studied for use in photoresistors; they contained linking components obtained according to the procedure shown in Fig. 2.7.

Another example of obtaining a promising monomer is the synthesis of tetra(2-cyanoethyl)glycoluril **15** with 61 % yield [56], which was obtained through the interaction of acrylonitrile and glycoluril in a water environment in the presence of diazabicycloundecene (DBU) as a base (Fig. 2.8).

Promising outcomes of polyfunctional polymer precursor synthesis are shown in the patent [57], where glycoluril **1** reacts with glycidylacrylate in 1-methoxy-2-propanolacetate (PGMEA) at 50 °C, giving tetrasubstituted glycoluril **16** (Fig. 2.9).

New glycoluril derivatives with sulfonic acid marks are impressive [58], particularly glycoluriltetrakis(butane-1-sulfonic acid) **17** in the shape of nanosized particles (Fig. 2.10). It was proven that this new nanostructured substrate is an effective catalyst for new spiropyrane synthesis through the multicomponent condensation of isatin, naphthalene-1,2-diol or 2,5-dihydroxycyclohex-2,5-dien-1,4-dion and malononitrile (or 1,3-dicarbonyl compound) in boiling water.

Glycoluril **1** cycloamination products were identified using *N,N*-bis (methoxymethyl)alkaneamines and $SmCl_3 \cdot 6H_2O$ as catalysts (Fig. 2.11). Reaction products were separated from the formed mixture by column chromatography using silica gel as a sorbent [59].

3,7,10-trioxo-2,4,6,8,9,11-hexaaza[3.3.3]propellane **19** has attracted interest in recent years – a cyclic carbamide derivative consisting of three condensed cycles connected by a common carbon–carbon bond, including a glycoluril fragment. Such [3.3.3]propellanes gained interest in the scientific community, having become the subject of a number of reviews [60,61].

Relatively recently [3.3.3]propellane with five nitrogen atoms in the structure was synthesized through a glycoluril derivative in stage (Fig. 2.12). The main point of this method is that the initial interaction of diethyl-2,3-dihydroxybutanedioate with carbamide in an acidic environment provides a bicyclization product, which is then tricyclized into [3.3.3]propellane **23** consecutively through intermediate bisamide in the presence of p-toluene sulfonic acid **23** [62].

Based on previously obtained results of the glycoluril diethyl ether nitration model reaction, the authors of [63] implemented such a shift to nitroderivatives of tetraoxopentaaza[3.3.3]propellanes **24a-b** (Table 2, Fig. 2.13). During these reactions, di- and trisubstituted nitrocompounds – 2,6-dinitro-3,7,9,11-tetraoxo-2,4,6,8,10-pentaaza[3.3.3]propellane **24a** and 2,6,10-trinitro-3,7,9,11-tetraoxo-2,4,6,8,10-pentaaza[3.3.3] propellane **24b** – were obtained in yields of 61 % and 53 %, respectively. The range of performed research did not allow the synthesis of pentanitrosubstituted propellane. Reactions were performed at room temperature for 10–12 h; then, the reaction mixture was poured on ice and filtered.

Another approach to [3.3.3]propellane was shown in the study [64] – a method of obtaining [3.3.3]hexaazapropellane structure with six NH groups was developed (Fig. 2.14).

In the study [65], uric oxide **25** was used as the initial compound; it was oxidized under $Na_2S_2O_8$, which caused the formation of 1,5-diaminoglycoluril **26**. The following tricyclization stage was performed successfully using di-*tert*-butylcarbonate (Boc_2O), forming intermediate product **27** at room temperature. The final stage of protective Boc-group removal led to final product **19** formation. It should be noted that two-stage synthesis can be performed without intermediate formation of **27**, and structures **27** and **19** were confirmed by X-ray diffraction analysis.

Considering the experimental data, more successful results were

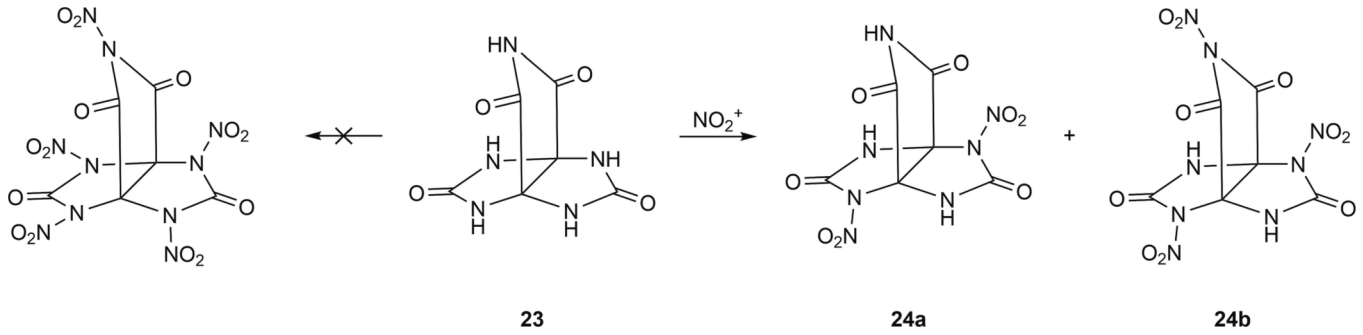


Fig. 2.13. Nitration of 3,7,9,11-tetraoxo-2,4,6,8,10-pentaaza[3.3.3]propellane.

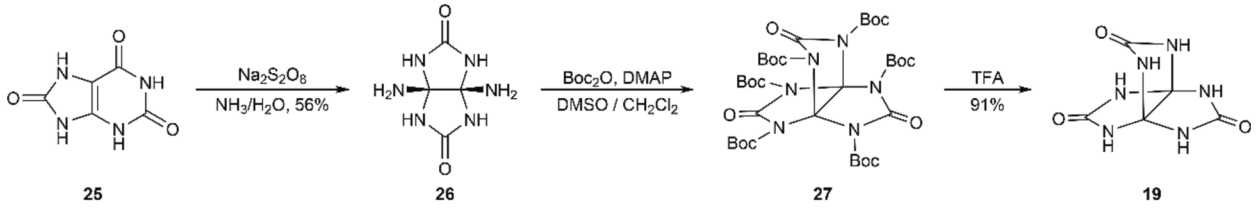


Fig. 2.14. Synthesis of hexaazapropellane **19**.

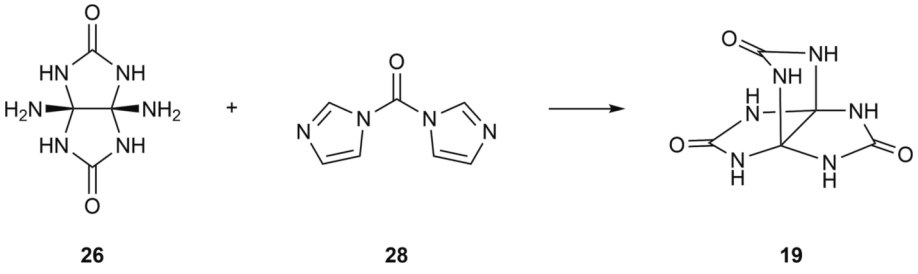


Fig. 2.15. Synthesis of propellane **19** using carbonyldiimidazole.

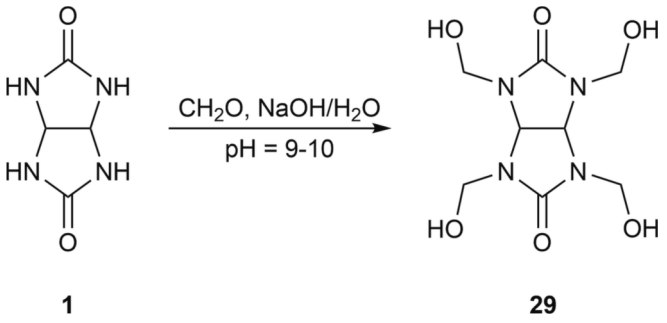


Fig. 3.1. Synthesis of THMGU.

Table 3
Properties of THMGU.

Parameter	Data
Melting point, °C	135–136
Solubility	Insoluble in hydrocarbons, alcohols, ketones, esters Slightly soluble in DMF, DMSO Soluble in H_2O, acids
IR-spectrum, cm^{-1}	3337 (OH); 1675 (C = O)
^1H NMR (DMSO-d_6)	5.97 (4H, OH)5.51 (2H, CH)4.70 (2H, CH_2)
^{13}C NMR (DMSO-d_6)	157.48 (C = O)87.03 (CH)65.10 (CH_2)

achieved in the study [66], which shows a one-stage way of obtaining **19** through carbonyldiimidazole **28** at 15–20 °C. Final product **19** was separated by acetone descension with a yield of 85 % (Fig. 2.15).

A series of studies [67,68] were aimed at finding ways of functionalizing 3,7,10-trioxo-2,4,6,8,9,11-hexaaza[3.3.3]propellane. During the research, methods for obtaining hexaalkyl derivatives of 3,7,10-trioxo-2,4,6,8,9,11-hexaaza[3.3.3]propellane (methyl-, ethyl-, propylderivatives) and mono- and dinitroderivatives of 3,7,10-trioxo-2,4,6,8,9,11-hexaaza[3.3.3]propellane were developed. It was found that complete acetylation of 3,7,10-trioxo-2,4,6,8,9,11-hexaaza[3.3.3] propellane proceeds in two stages through the formation and separation of intermediate 2,6-di- and 2,6,9-triacetylsubstituted derivatives of 3,7,10-trioxo-2,4,6,8,9,11-hexaaza[3.3.3]propellane.

4. *N*-hydroxymethylglycoluril-based macrocycle synthesis

4.1. General information about tetra-*N*-hydroxymethylglycoluril

N-hydroxylalkylderivative glycolurils are traditionally obtained through reaction with aldehydes, of which the most synthetically important is the parent 2,4,6,8-tetrahydroxymethyl-2,4,6,8-tetraazabicyclo[3.3.0]octan-3,7-dione (tetra-*N*-hydroxymethyl glycoluril, THMGU) **29**, which is obtained through a typical reaction of glycoluril **1** formylation [24] in an alkaline environment (Fig. 3.1).

Currently, THMGU is widely used as a linking agent for obtaining glycoluril-formaldehyde resins [69] and high-quality thermosetting

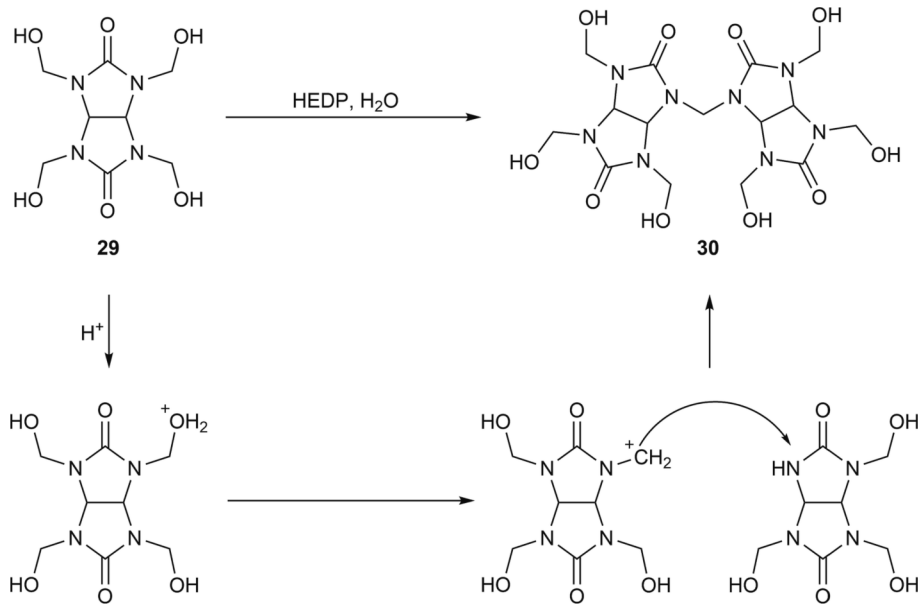


Fig. 3.2. Dimerization of THMGU **29** in the presence of HEDP.

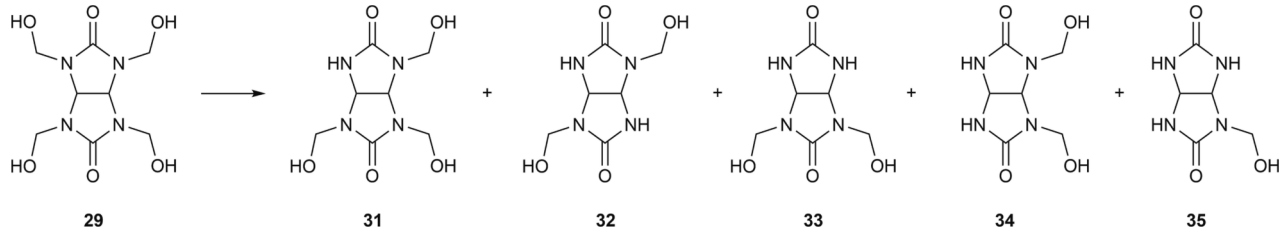


Fig. 3.3. Consecutive elimination of formaldehyde from THMGU **29.**

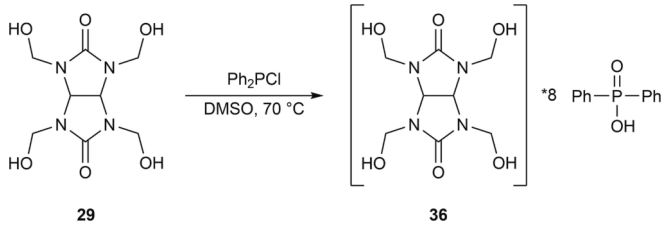


Fig. 3.4. Product of interaction of THMGU **29** with diphenylchlorophosphine.

coatings [70] and for supramolecular object synthesis [71], as well as a bactericidal agent for aqueous compositions [72].

THMGU is widely used as a linking agent in different fields [70,73,74]. For example, it was suggested to use an ethylene–vinyl chloride emulsion containing 4 to 10 mass percent THMGU as a linking agent for filter paper. It is said that paper soaked in this emulsion maintains strength and flexibility even when exposed to hot oil.

The authors of the patent [75] suggested a microencapsulation system using THMGU for various carboxamide compounds in different industry fields: antipyrenes, pharmaceuticals, cosmetics, etc. The authors give most attention to the agrochemical area.

In [76], THMGU was used as a linking agent for the creation of methylmethacrylate- and acrylamide-based macroporous polymers.

THMGU is a white powder, very soluble in water and DMF and poorly soluble in most other organic solvents (Table 3). When stored with air contact, THMGU tends to detach from formaldehyde, thus gaining a typical yellow color. In water solution at pH = 4–8, THMGU undergoes demethylolation until reaching equilibrium: approx. 3.6 hydroxymethyl groups per glycoluril molecule with 0.4 parts of free formaldehyde. A pH over 8.8 promotes demethylolation even more. For example, at pH = 11, the amounts of hydroxymethyl groups and free formaldehyde are approximately equal [77].

After studying properties **29** in the presence of 1-hydroxyethylidene-1,1-diphosphonic acid (etidronic acid, HEDP), it was found that the substance dimerizes, yielding product **30,** and with a longer period of time, there is no further oligomerization (Fig. 3.2). This feature is highly irregular and selective, as using mineral acids leads to the formation of macrooligomerization products [71].

Dimer **30** was also separated in a different experiment with heating to 60 °C a water solution of glycoluril **1** with excessive formaldehyde (pH = 3,4) [78].

It should be noted that dimer **30** obtained through condensation is evidence that supramolecule formation in this case is difficult, as hydroxymethyl end groups “block” further condensation processes due to the lack of reaction partners with vacant NH groups. This can explain the fact that with longer reaction times and high temperatures, there are no insoluble residues, proving the formation of macromolecular systems.

The study [79] found that THMGU **29** is unstable and tends toward dehydroxymethylation products. Products of its step-by-step dehydroxymethylation (Fig. 3.3) were identified by HPLC and 1D/2D NMR spectroscopy.

The most stable product of hydrolytic destruction is tris(hydroxymethyl)glycoluril **31**, which can be caused by peculiarities of intramolecular interaction formation in THMGU **29**. Further dehydroxymethylation with the formation of glycoluril di- and monoderivatives **32–35** (Fig. 3.3) occurs under much harsher conditions.

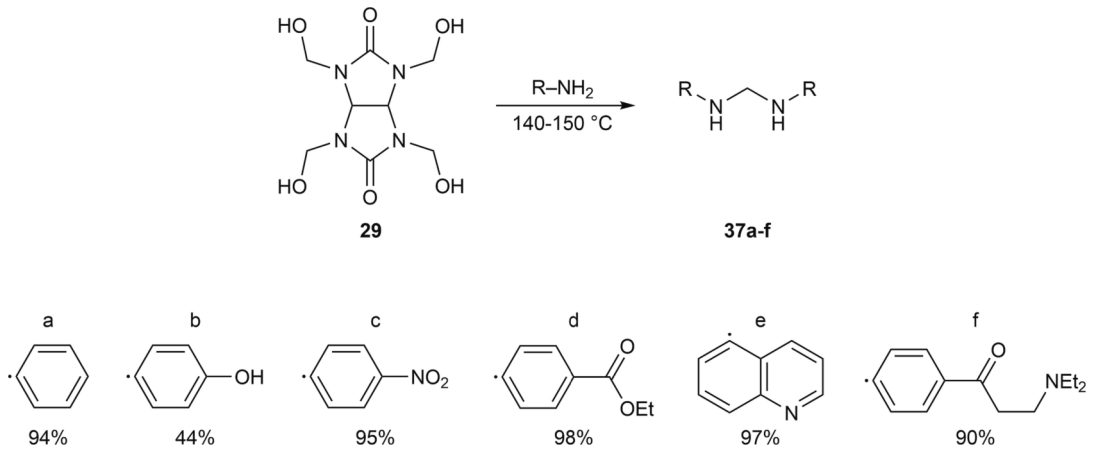


Fig. 3.5. Synthesis of aminals **37a-f** from **29.**

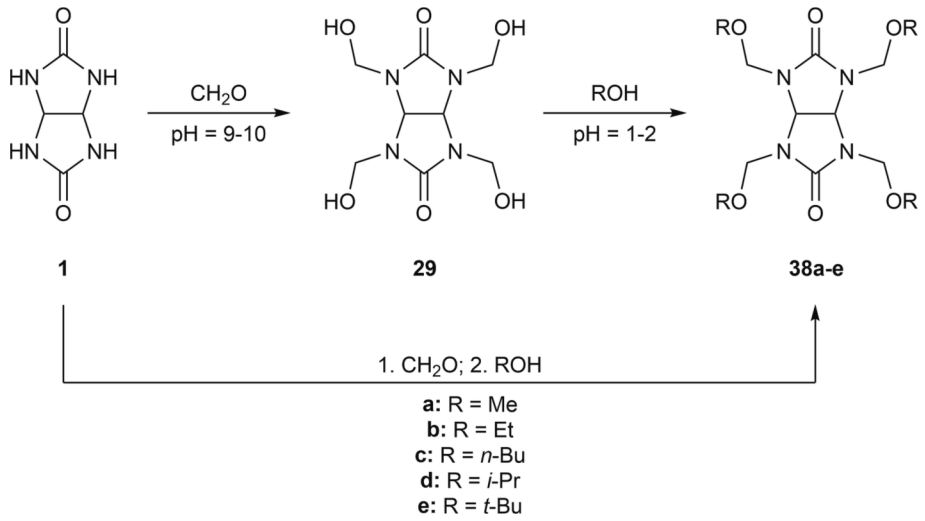


Fig. 3.6. Synthesis of tetra(alkoxymethyl)glycolurils **38a-e.**

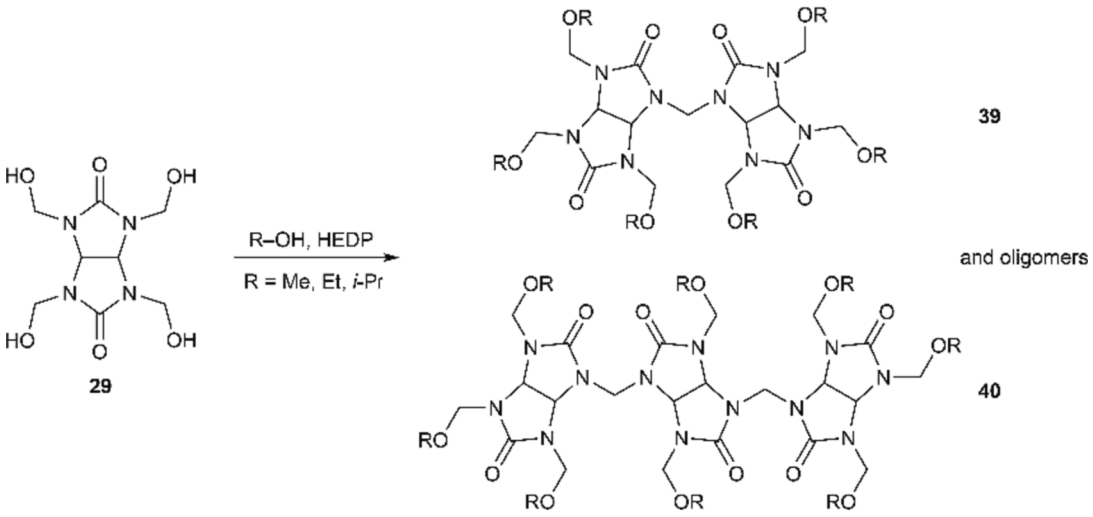


Fig. 3.7. Oligomerization of THMGU **29** under HEDP.

It should be noted that complexes **29** with HEDP were not separated from the reactin mixture. However, in reaction with diphenylchlorophosphine **29** gives complex product **36** (Fig. 3.4), which was obtained in a DMSO environment at room temperature for 3 h [80]. After the reaction, white crystalline sediment dissolved poorly in water and did not dissolving in organic solvents.

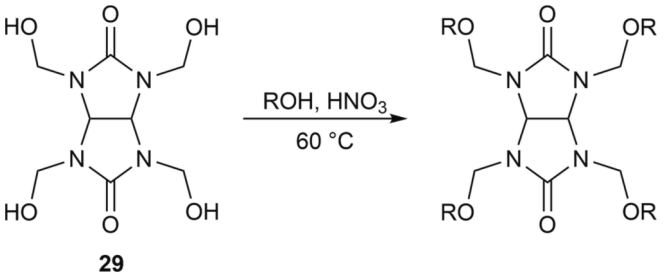


Fig. 3.8. *N*-alkoxymethylglycoluril synthesis.

It is interesting that considering the tendency for elimination of tetrasubstituted glycoluril **29** formaldehyde, it was suggested to synthesize aminals **37a-f** (Fig. 3.5) with yields of 44–98 % [81].

Tetra(hydroxymethyl)glycoluril **29** is a polyfunctional alcohol, and a number of ethers are obtained from it in acidic catalysis (HCl, HBr) – tetra(alkoxymethyl)glycolurils **38a-e,** which are widely used as linking agents in obtaining polymers [82]. In addition, there are examples of obtaining tetraether compounds [83] using **1** as an initial base, skipping the stage of separating **29** (Fig. 3.6).

The same study shows that after replacing mineral acids with HEDP in reactions involving glycoluril **1** as an initial substrate, the latter rearranged into hydantoin. Different results were achieved using THMGU**29** – instead of expected ether products **38a-e,** the process included formation of oligomeric Compounds **39–40** with terminal arrangement of alkyl groups - derivatives of methyl, ethyl and isopropyl alcohol (Fig. 3.7).

To explain the results of oligomer **39–40** formation, a mechanism assuming intermediate dehydroxymethylation in the water environment of initial substrate **29** was suggested. With longer reaction times, oligomeric chains increase, as there are poorly soluble residues of unknown structure.

4.2. *Reactions of glycoluril N-hydroxymethyl derivatives*

THMGU **29** reacts with alcohols if heated with mineral acids, forming respective tetraalkoxymethylglycolurils. The study [84] gives examples of synthesizing ethoxy- and methoxymethylglycolurils, and an extended line of **29** reactions with various alcohols is given in the patent [55]. A typical approach is exposing suspension **29** to the respective alcohol with nitric acid at 60 °C (Fig. 3.8).

Depending on the method of product separation and the alcohol involved in the reaction, either liquid tars or solid substances with high melting temperatures can be formed. Alkoxyglycoluril tars are widely used for surface treatment, and they have a number of advantages over melamine–formaldehyde tars, such as resistance to acid hydrolysis and UV rays [85].

The hydroxylation reaction speed depends directly on the amount of catalyst added. The direct reaction is faster in acidic media, but the reverse reaction speed is much lower in acidic environments. However, after being in an acidic environment for a long time, the glycoluril tetrahydroxymethyl derivative may condense in the form of a tetracyclic diether [86]. Conversion of *N*-hydroxymethylglycolurils containing substitutes R_1 and R_2 into respective diethers is possible at room temperature. The presence of more volume substitutes increases the cyclocondensation reaction activation energy due to steric effects: for example, diphenylglycoluril diether can be obtained only in the case of reaction mixture heating (Fig. 3.9).

At low pH (1–2), there is a condensation reaction (Fig. 3.10) with the formation of oligomers connected by methylene bridges [8]. There is no information on the possibility of similar processes in alkaline environments.

Apart from glycoluril-formaldehyde tars, glycoluril alkoxoderivatives can also be used in new material creation. For example, tetrakis (methoxymethyl)glycoluril **41** is used as a binding agent in the creation of a three-component negative photoresist from molecular glass [87]. Photoacid is generated by mixture irradiation and catalyzes the linking

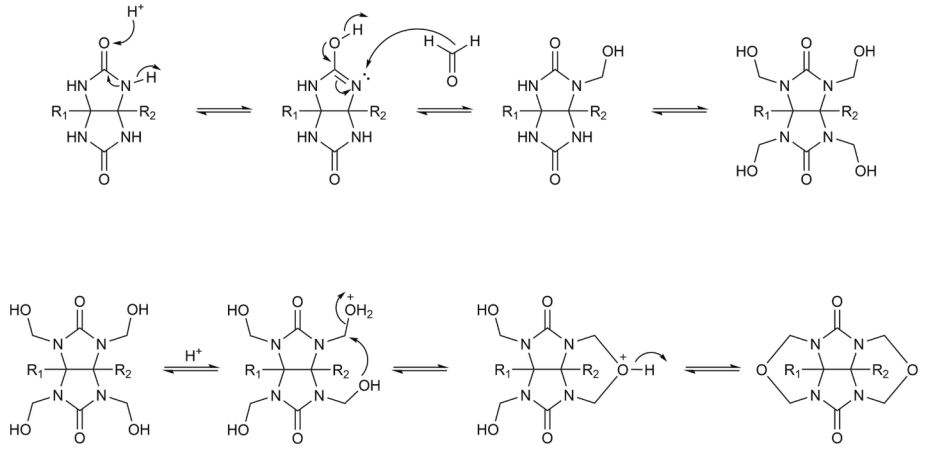


Fig. 3.9. Transformations in the glycoluril-formaldehyde reacting system in an acidic medium.

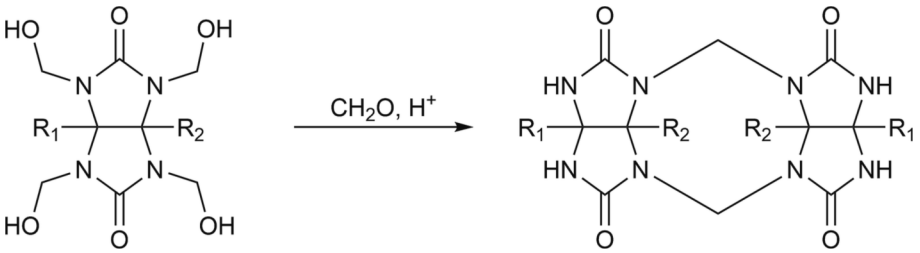


Fig. 3.10. Transformations in the glycoluril-formaldehyde reacting system in strong acidic medium.

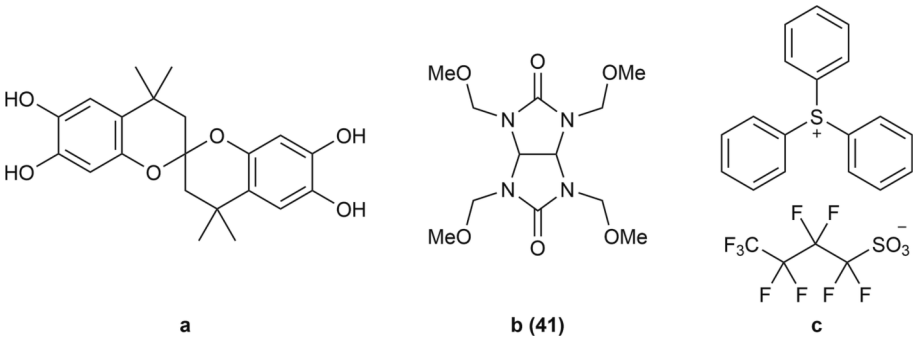


Fig. 3.11. Three-component molecular glass negative photoresist: a – monomer, b – tetrakis(methoxymethyl)glycoluril **41**, c – acid catalyst.

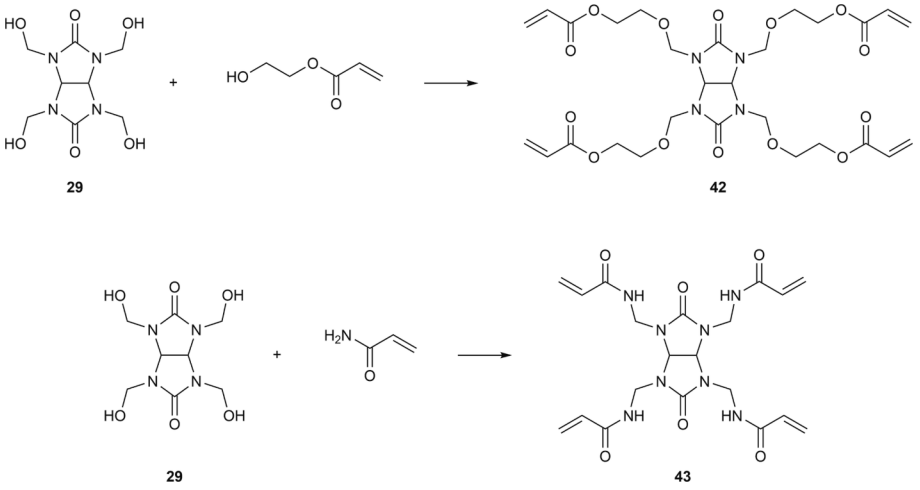


Fig. 3.12. Reaction of THMGU **29** with hydroxyethylacrylate and acrylamide.

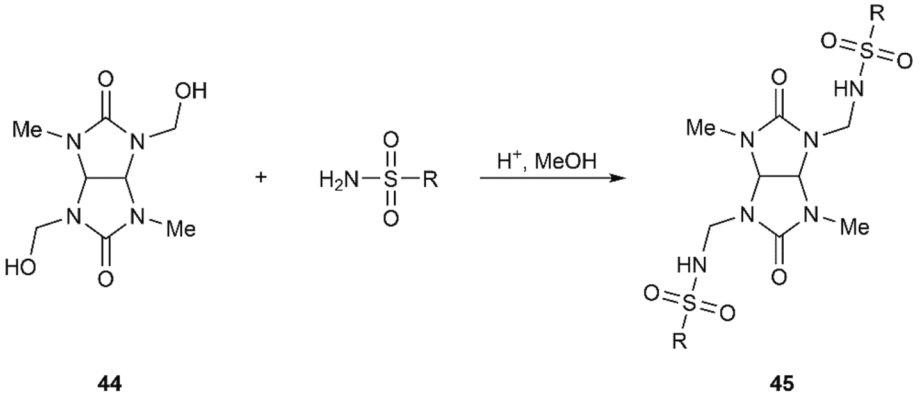


Fig. 3.13. Condensation of glycoluril derivative **44** with sulfonamide.

process between **41** and monomer hydroxylic groups (Fig. 3.11).

When reacting with alcohols containing double bonds, **29** forms aminoplastics with side α,β-unsaturated carbonyl groups. The study [82] described reactions of **29** with hydroxyethylacrylate and acrylamide (Fig. 3.12) with the formation of respective products **42**–**43**.

The most preferred option is when **29** is reacted with a mixture of hydroxyethylacrylate and acrylamide, which leads to stable product formation. It was found that after mixing such products with other aminoplastics with side α,β-unsaturated carbonyl groups and single-stage resins, the conversion rate during cross-linking increased.

Several studies [88–90] have researched reactions of α-ureidoalkylation of sulfonamides, sulfonamides and *N,N*'-dialkylsulfamides using mono-, di- and tetra-*N*-hydroxymethylglycolurils.

Sulfonamide condensation with glycoluril **44** containing one hydroxymethyl group is shown in Fig. 3.13, with 2-hydroxymethyl-4,6,8-trimethylglycoluril and benzene sulfonamide. This reaction was completed in 1 h in boiling methanol in the presence of hydrochloric acid. Sulfonamides with 2,6-dihydroxymethylglycoluril **44** in these conditions give 2,6-bis(arylsulfonylaminomethyl)glycolurils **45** with yields of 27–50 %.

Sulfamide condensation with 2,8-bis(hydroxymethyl)glycolurils **34** leads to the formation of tricyclic dioxides (Fig. 3.14).

Condensation of **29** with *N,N*'-dimethylsulfamide in water and an acidic environment (pH 1) leads to the formation of tetracyclic

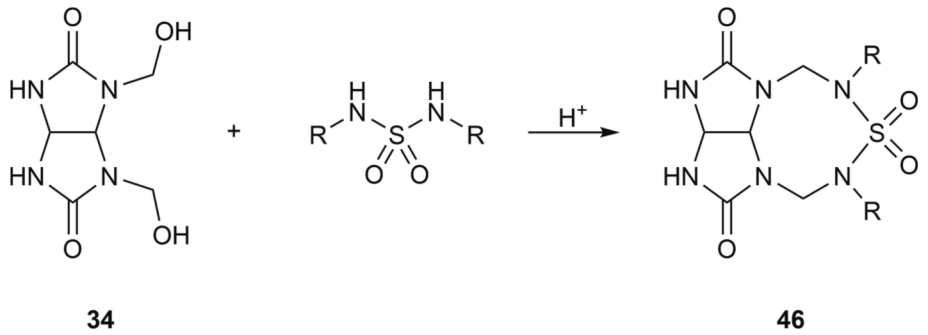


Fig. 3.14. Condensation of 2,8-bis(hydroxymethyl)glycoluril **34** with sulfamides.

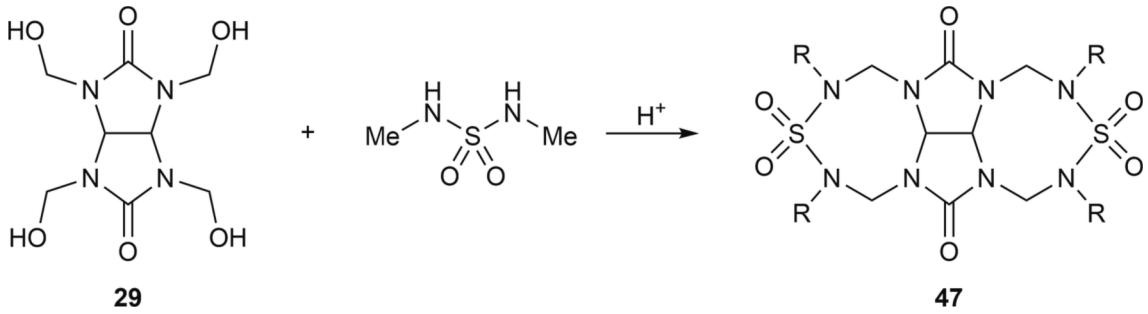


Fig. 3.15. Condensation of THMGU **29** with *N,N'*-dimethylsulfamide.

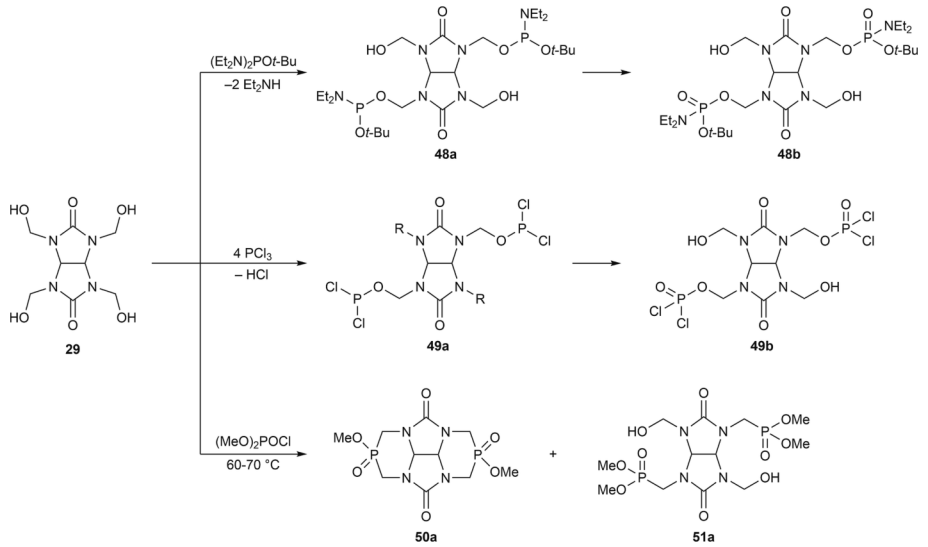


Fig. 3.16. Phosphorylation of THMGU **29.**

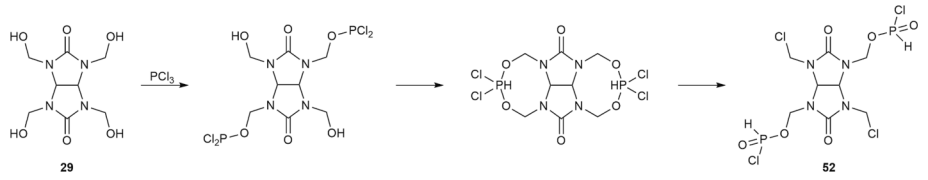


Fig. 3.17. Interaction of THMGU **29** with PCl_3.

compounds (Fig. 3.15).

Phosphorylation of tetra(hydroxymethyl)glycoluril **29** with tetraethyldiamido-*tert*-butylphosphite [91] leads to the formation of an oleiferous product – 2,6-di-(*N*-diethylamidohydroxymethylphosphato)-2,4,6,8-tetraazobicyclo[3.3.0]octan-3,7-dione **48b** through the formation of intermediate Compound **48a** (Fig. 3.16). Interaction of **29** with phosphorus trichloride leads to separation of the yellow crystalline substance – 2,6-di-(*N*-methylchlorophosphato)-4,8-chloromethyl-

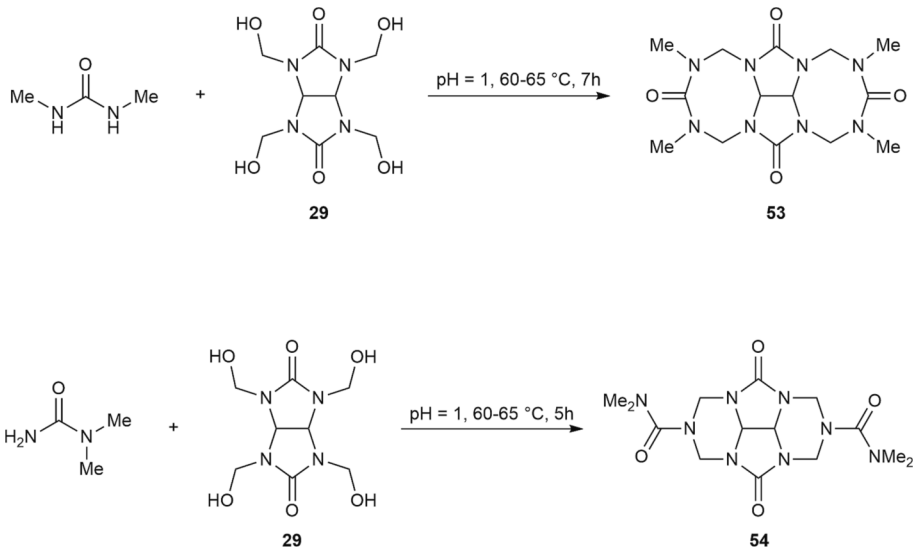


Fig. 3.18. Ureidoalkylation of dimethylureas.

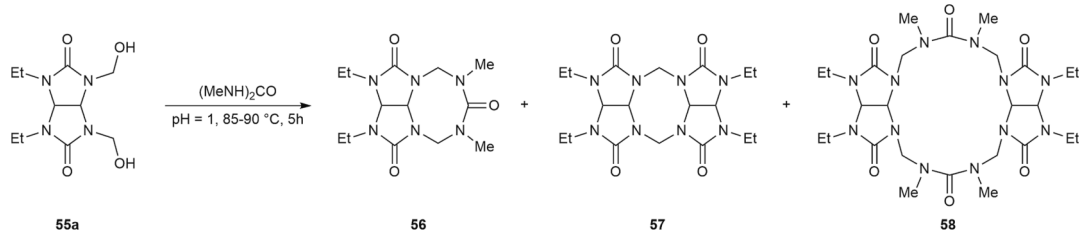


Fig. 3.19. Reaction of glycoluril derivative **55a** with 1,3-dimethylurea.

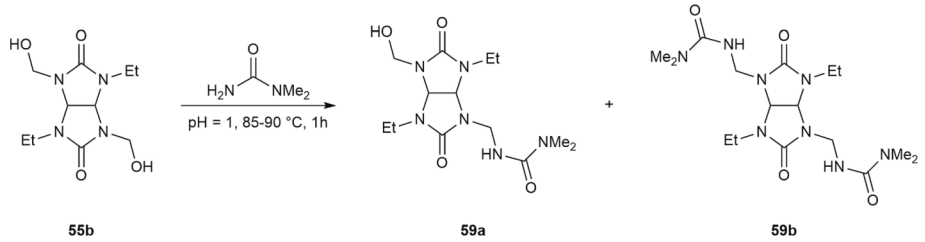


Fig. 3.20. Reaction of glycoluril derivative **55b** with 1,1-dimethylurea.

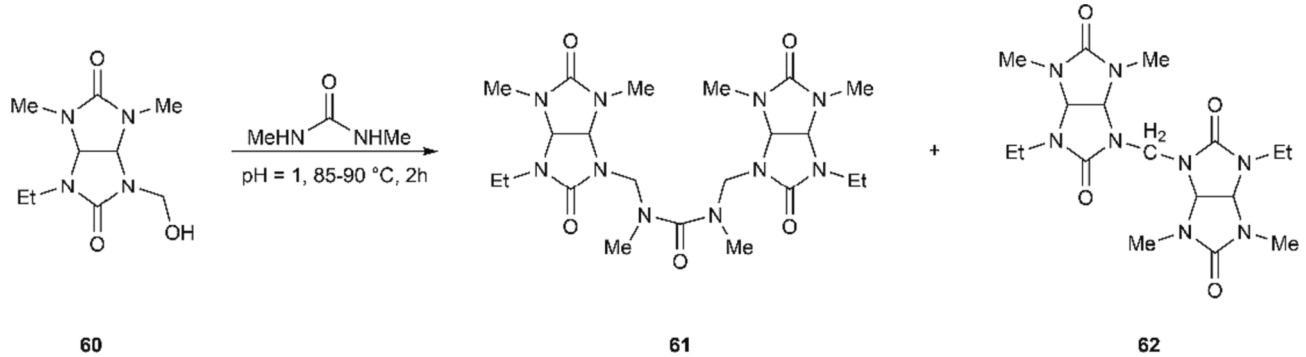


Fig. 3.21. Ureidoalkylation of glycoluril derivative **60.**

2,4,6,8-tetraazobicyclo[3.3.0]octan-3,7-dion **49b** – product obtained after phosphoric fragment oxidation in Compound **49a** to the quinquevalent state. Reaction of **29** in an absolute benzene with two dimethoxychlorophosphate and pyridine equivalents as hydrogen chloride acceptors led to the formation of mixtures **50a** and **50b**, and the reaction proceeded with intense heat emission.

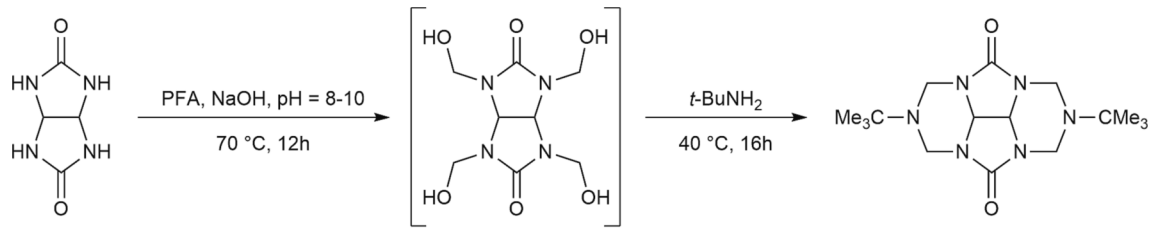


Fig. 3.22. Cycloaminomethylation of glycoluril (PFA = paraformaldehyde).

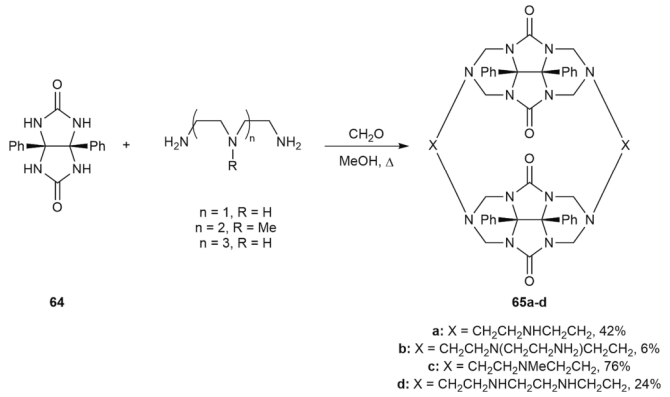


Fig. 3.23. Macrocyclic polyamines based on diphenylglycoluril **64.**

Pooled analysis of chemical shifts in NMR spectra ^{31}P and ^{13}C of bicyclic biscarbamide phosphatives was performed in the study [92]. The phosphorus trichloride effect on **29** leads to a tetracycle containing two eight-membered rings, which then open with the formation of 2,6-di (*N*-methylchlorophosphato)-4,8-chloromethyl-2,4,6,8-tetraazobicyclo [3.3.0]octan-3,7-dione **52** (Fig. 3.17).

Glycoluril hydroxymethyl derivatives can be used for carbamide α-ureidoalkylation with the formation of bi and polycyclic systems [88]. As with sulfonamides, tetra-*N*-hydroxymethyl-, 2,8-*cis*-bis-(hydroxymethyl)-, 2,6-*trans*-bis(hydroxymethyl)- and monohydroxymethylglycolurils were used in water solution at pH = 1 for condensation with different carbamides. The impact of temperature and reaction time on the initial glycoluril conversion rate was also studied.

α-Ureidoalkylation of 1,3- and 1,1-dimethylcarbamides using **29** leads to the formation of tetracyclic condensed polyazasystems **53**–**54** containing four carbamide fragments (Fig. 3.18).

As a result of the reaction of *cis*-bis-hydroxymethylglycoluril **55a** with symmetrical 1,3-dimethylcarbamide, in addition to expected tricyclic product **56**, two pentacyclic systems **57**–**58** was also formed (Fig. 3.19).

During the reaction of *trans*-bis(hydroxymethyl)-glycoluril **55b** with 1,1-dimethylcarbamide in an equimolar ratio, there is selective condensation through one of the hydroxymethyl groups (Fig. 3.20) with the formation of only 3 % of the side disubstituted product. Use of stoichiometric ratios of glycoluril **55b** and carbamide in the same ratios leads to yields of 10 % through mono-**59a** and 20 % through disubstituted **59b** products.

α-Ureidoalkylation of 1,3-dimethylcarbamides with mono(hydroxymethyl)glycoluril **60** also leads to the formation of two products: ureidobisglycoluril **61** and 8,8′-methylenebis(6-ethyl-2,4-dimethylglycoluril) **62** (Fig. 3.21).

The glycoluril cycloaminimethylation reaction is of high interest for the synthesis of bioactive tetracyclic compounds. In addition, such compounds are used as light stabilizers, stabilizers in the production of plastics, coatings and organic materials protecting from oxygen and heat.

Glycoluril cycloaminimethylation can be performed in an easier and more efficient way with formaldehyde in the presence of catalytic amounts of NaOH for the formation of tetrakis(hydroxymethyl)glycoluril and its instant cyclization with an appropriate amine (Fig. 3.22). Such approaches were used in [93] with example of *tert*-butylamine and with monoethanolamine [94]. These studies state the possibility of using

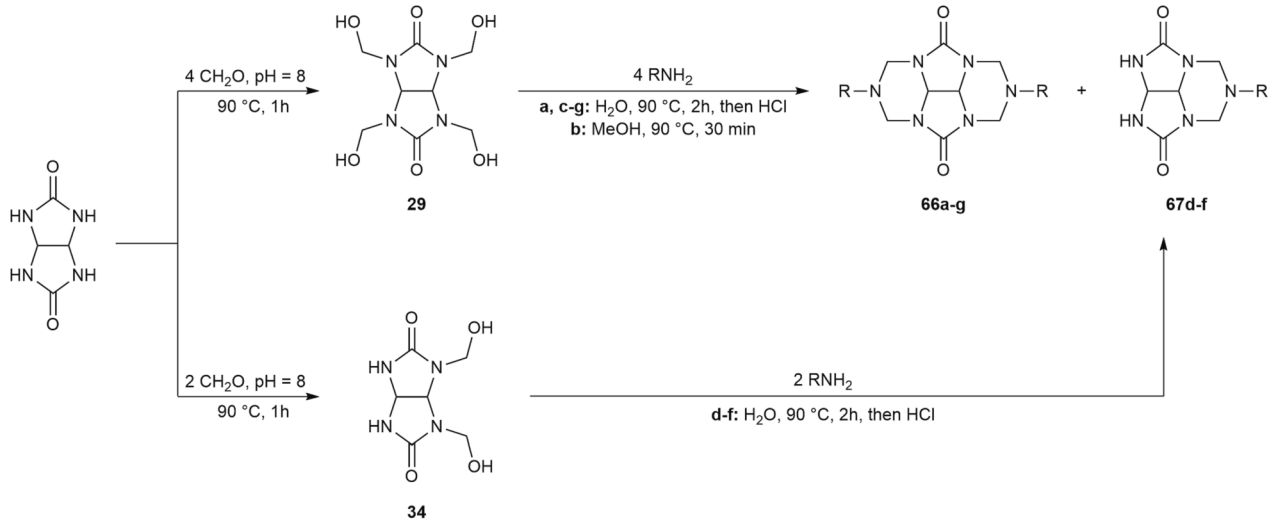


Fig. 3.24. Synthesis of tetracyclic compounds based on THMGU **29.**

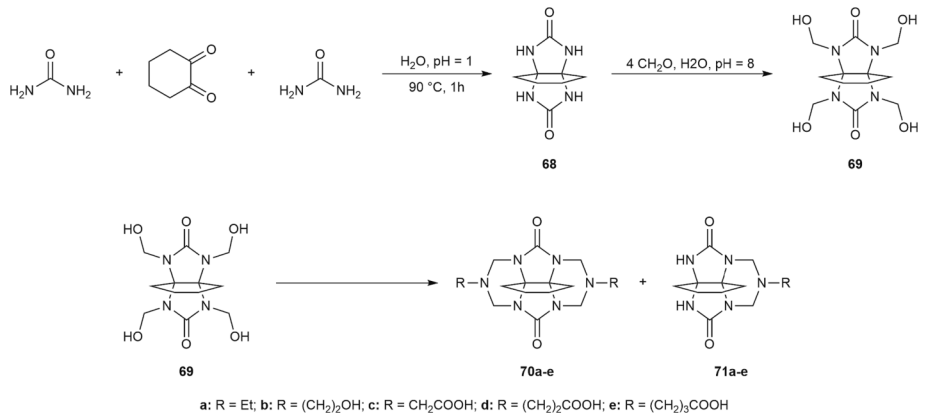


Fig. 3.25. Synthesis of hexacyclic and pentacyclic compounds from urea.

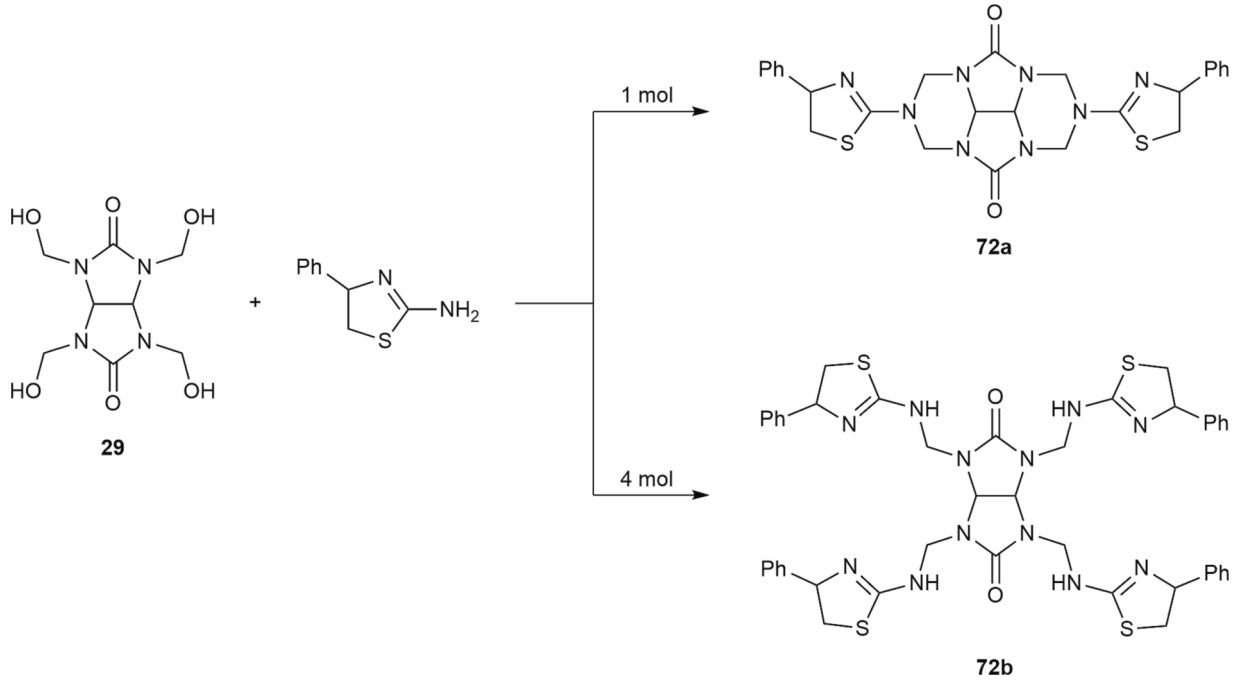


Fig. 3.26. Condensation of THMGU with 2-amino-4-phenylthiazole.

glycoluril for aminogroup protection (as in a strongly alkaline environment, *N*-aminomethylated glycoluril derivatives decompose through N-CH_2 bonds).

Glycoluril or its derivative hydroxymethylation with formaldehyde or paraformaldehyde with instant Mannich cyclization is widely used in the synthesis of molecular clips, molecular scaffolds and other polycyclic compounds. For example, new macrocyclic polyamines **65a–d** and macrocycles [95] were synthesized by diethylentriamine (and triethylentetraamine) condensation with formaldehyde and diphenylglycoluril **64** (Fig. 3.23).

Reactions of glycoluril with aliphatic amines and potassium salt amino acids were studied in detail in [89]. As a result of these reactions, the authors performed the synthesis of optically pure polycycles by the interaction of (*S*)-α-amino acids with THMGU and 1,5-butano-THMGU. Optimal conditions for THMGU-based tetracycle synthesis were found: the reaction proceeded for two hours in water at 90 °C with a yield of 65–90 % (Fig. 3.24). In some cases, for example, with hexylamine, methanol is an efficient solvent. In this case, the reaction takes 30 min with 90 % yield. Formed tetracycles always contain impurities of respective tricyclic compounds that can be synthesized when using a lower ratio of formaldehyde and amino acid to glycoluril. However, *N*-hydroxymethylglycioluril and amino acid oligomers are formed in side reactions.Fig 3.25.Fig 3.26.

Based on the tetra-*N*-hydroxymethyl derivative of 1,5-butanoglycoluril, the authors synthesized hexa- and pentacycles in 43–87 % yield. Ethylamine, monoethanolamine and amino acids in the form of potassium salt water solutions were condensed with 1,5-butano-THMGU. Individual hexacycles **70a–e** and pentacycles **71b–c** were separated by fractional crystallization, and Compounds **71a**,**d–e** failed to separate individually.

Several studies [96,97] researched the reaction of condensation of THMGU **29** with 2-amino-4-phenylthiazole. Depending on the amount of added thiazole, different reaction products can be formed. At an equimolar ratio of initial reagents, tetracycle **72a** is formed, and excessive use of thiazole leads to the formation of **72b**.

The authors also found that **72b** can transform into **72a** with an almost quantitative yield, thus suggesting that Compound **72b** can be an intermediate in the synthesis of tetracycle **72a**. The single-step synthesis of **72a** from glycoluril through the Mannich reaction is characterized by low yield.

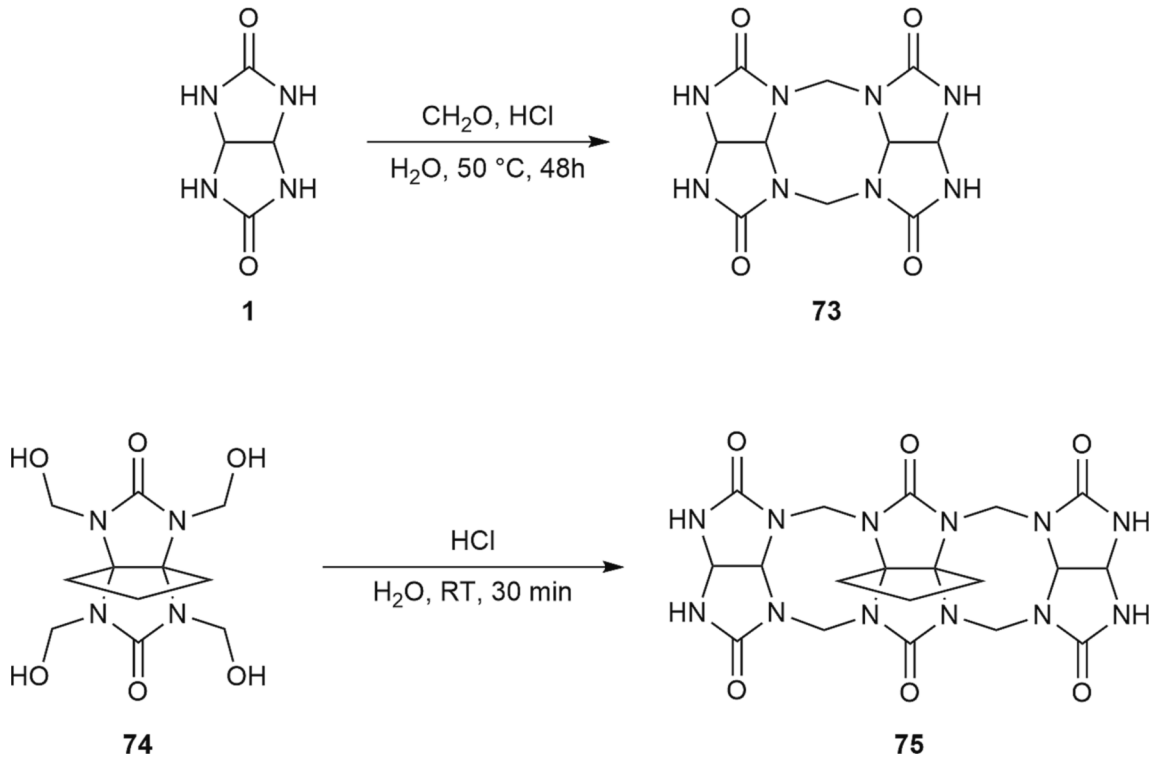


Fig. 3.27. Dimers and trimers of glycoluril derivatives as precursors for the synthesis of macrocyclic compounds.

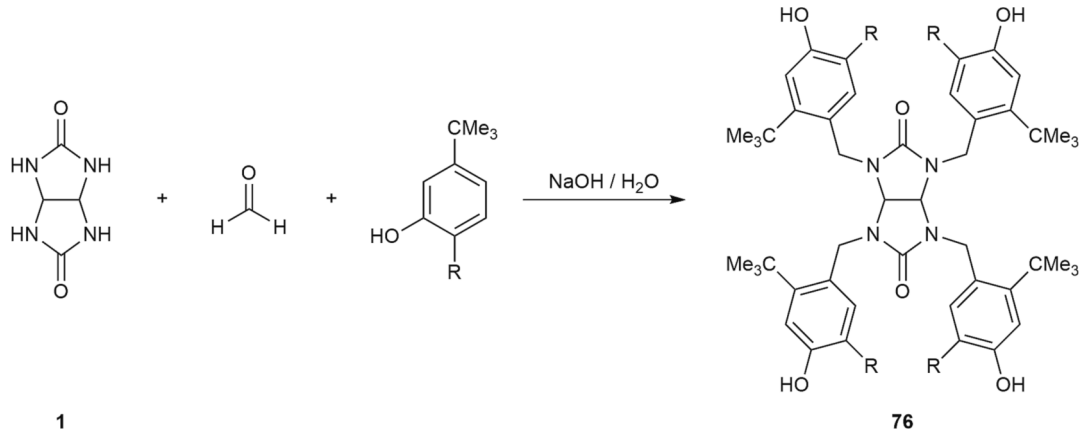


Fig. 3.28. Synthesis of stabilizers based on glycoluril **1.**

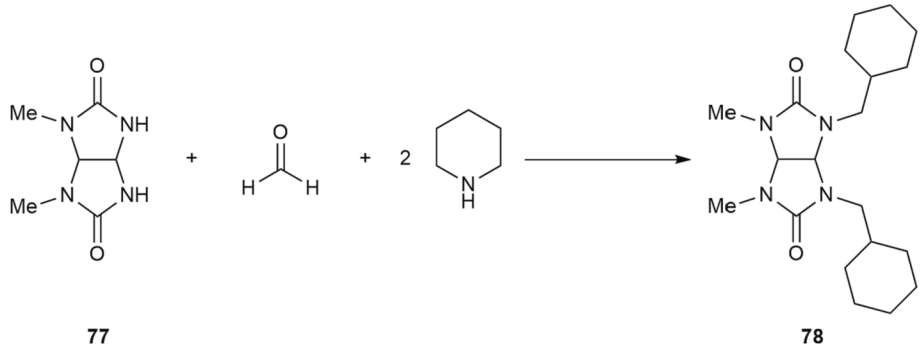


Fig. 3.29. Synthesis of glycoluril derivative **78.**

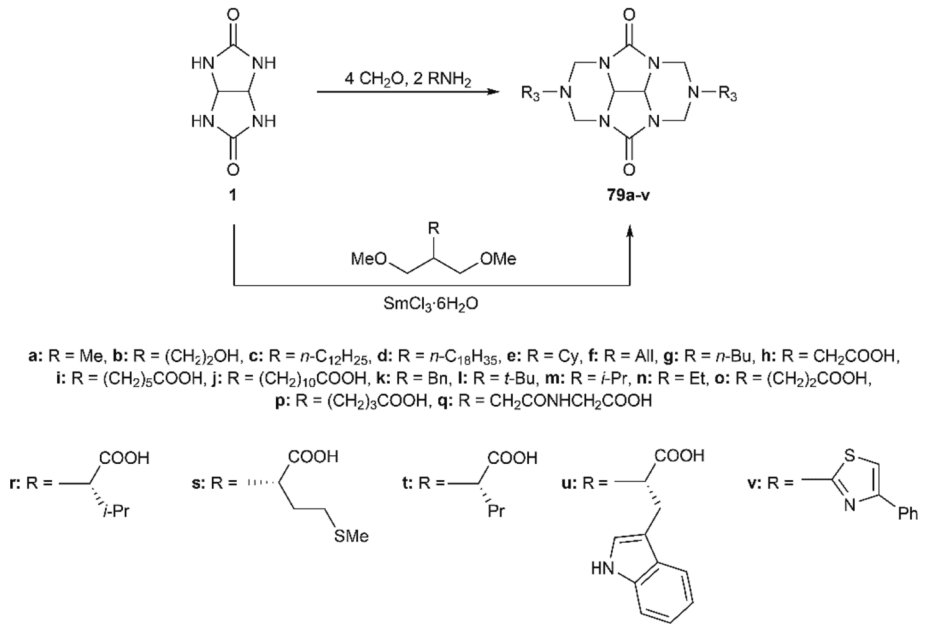


Fig. 3.30. Mannich reaction of glycoluril **1.**

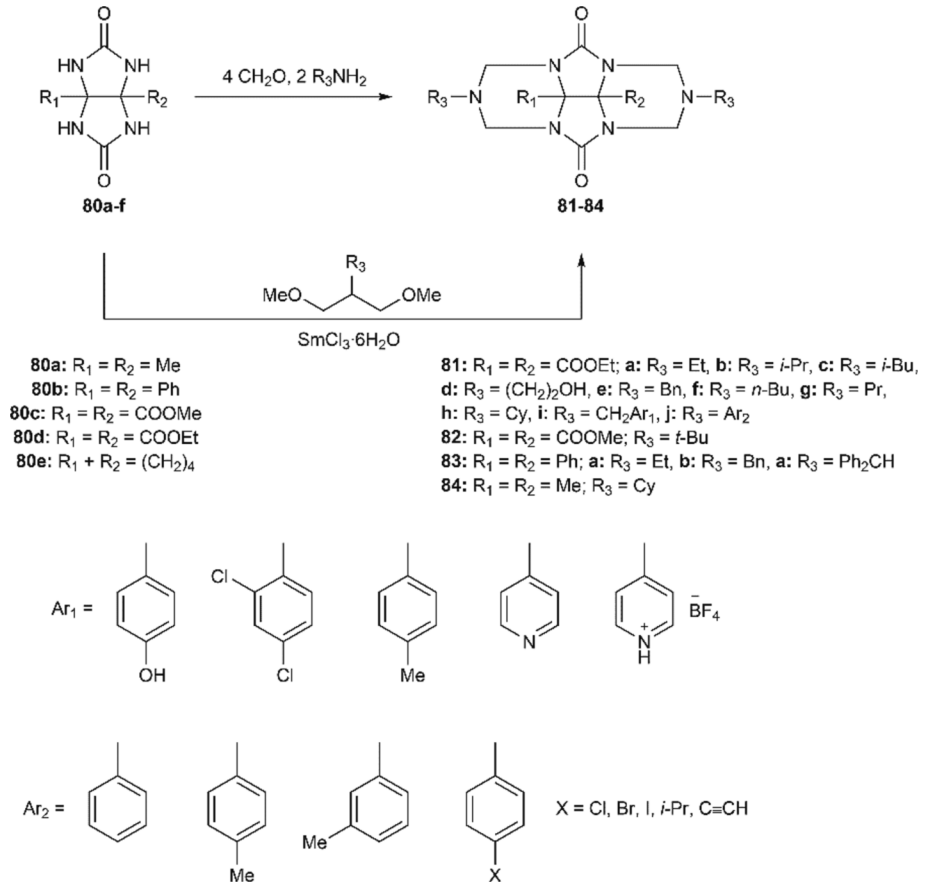
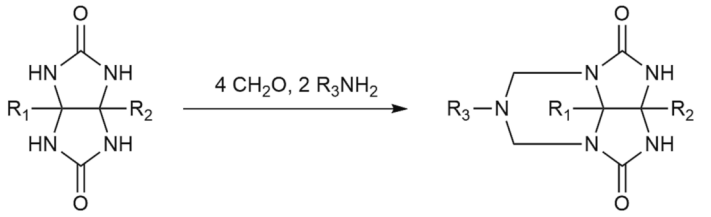


Fig. 3.31. Condensation of glycoluril derivatives **80a**–**e** with amines.

The reaction of glycolurils with formaldehyde became the basis for rapid progress in glycoluril condensed polycyclic derivative chemistry, such as cucurbiturils and bambusurils, which are interesting objects for supramolecular chemistry research [33]. In the case of changing the initial reagent ratio in formaldehyde reactions, dimers **73** and trimers **75** can be obtained (Fig. 3.27) as precursors in cucurbituril synthesis [98,99].Fig 3.28.

Through the Mannich reaction or gradually through intermediate THMGU **29** *N*-aminomethylated derivatives were synthesized, including tri- and tetracyclic condensed azaheterosystems [100,101].

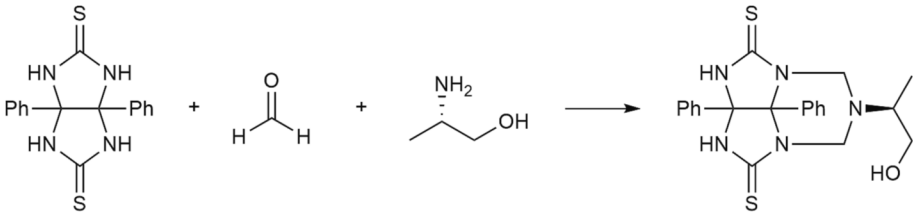


1; 80b, 80d **85-87**

1: $R_1 = R_2 = H$
80b: $R_1 = R_2 = Ph$
80d: $R_1 = R_2 = COOEt$

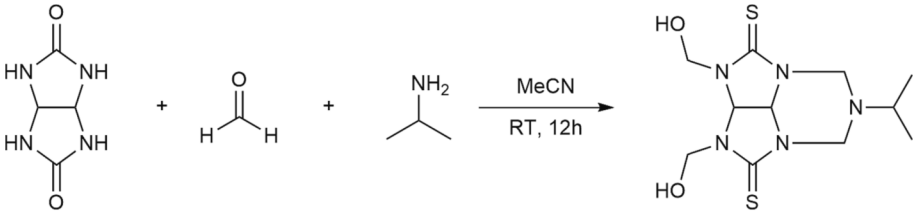
85: $R_1 = R_2 = H$; $R_3 = (CH2)_mCOOH$, **a:** m = 1, **b:** m = 2, **c:** m = 3
86: $R_1 = R_2 = Ph$; $R_3 = Et$
87: $R_1 = R_2 = COOEt$; **a:** $R_3 = (CH_2)_2OH$, **b:** $R_3 = Bn$,
c: $R_3 = p\text{-}Br(C_6H_4)CH_2$, **d:** $R_3 = Et$

Fig. 3.32. Condensation of glycoluril **1** and its derivatives **80b** and **80c** with amines.



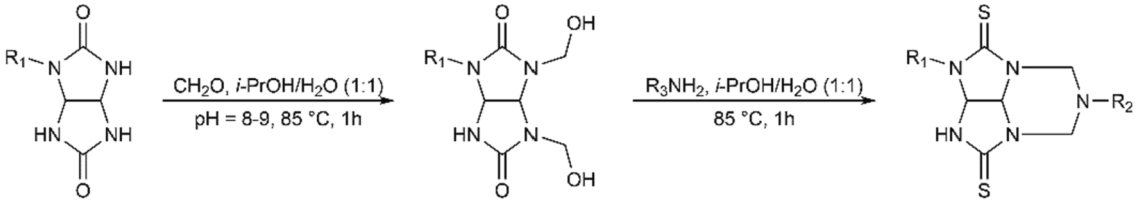
88 **89**

Fig. 3.33. Condensation of 88 with formaldehyde and (S)-2-aminopropan-1-ol.



1 **90**

Fig. 3.34. Condensation of glycoluril **1** with formaldehyde and isopropylamine.



91a: R_1 = *t*-Bu
91b: R_1 = Cy

92a: R_1 = *t*-Bu
92b: R_1 = Cy

93a–g: R_1 = *t*-Bu
94a–g: R_1 = Cy

93	**94**
a: R_2 = Et, 76%	**a:** R_2 = Et, 76%
b: R_2 = *n*-Pr, 70%	**b:** R_2 = *n*-Pr, 72%
c: R_2 = *n*-Bu, 74%	**c:** R_2 = *n*-Bu, 75%
d: R_2 = *s*-Bu, 75%	**d:** R_2 = *s*-Bu, 78%
e: R_2 = *t*-Bu, 70%	**e:** R_2 = *t*-Bu, 70%
f: R_2 = Cy, 84%	**f:** R_2 = Cy, 81%
g: $R_2 = (CH_2)_2OH$, 80%	**g:** $R_2 = (CH_2)_2OH$, 74%

Fig. 3.35. Condensation of glycoluril derivatives with formaldehyde and aliphatic amines.

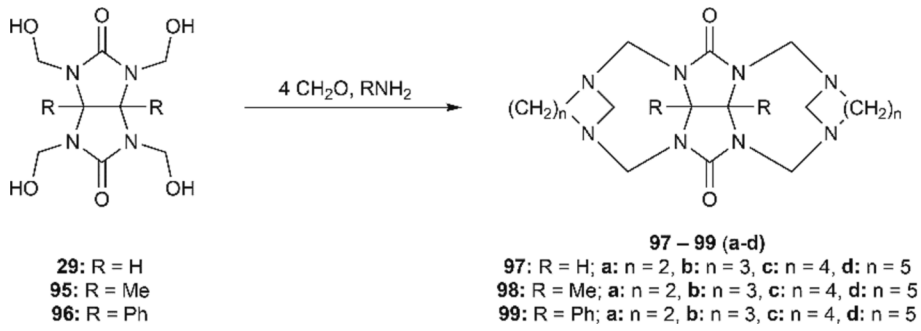


Fig. 4.1. Hexacyclic systems based on THMGU **29** and its derivatives.

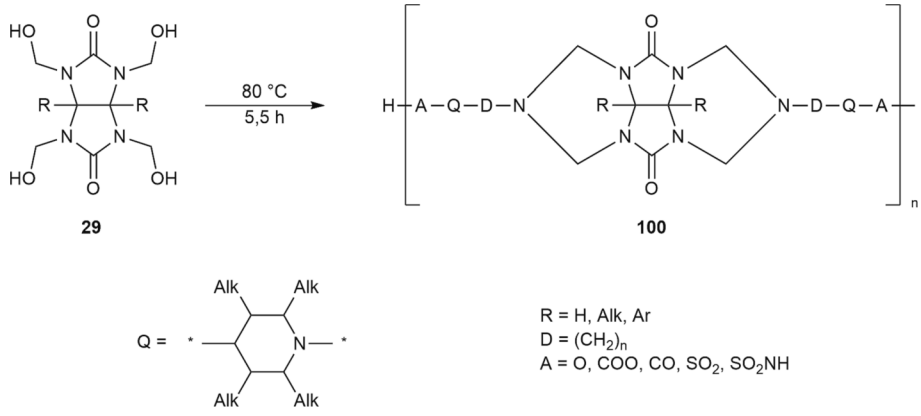


Fig. 4.2. Macrocyclic polymer based on THMGU **29**.

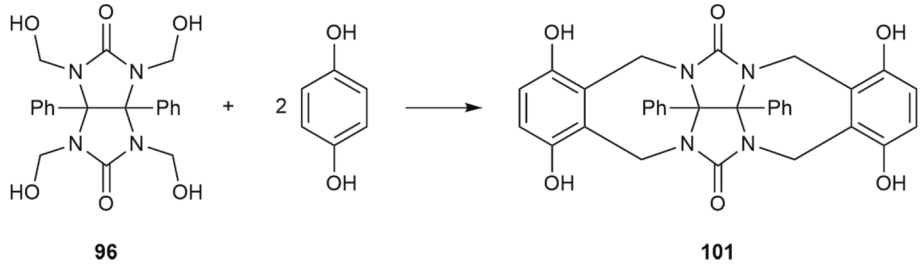


Fig. 4.3. Condensation of glycoluril derivative **96** with hydroquinone.

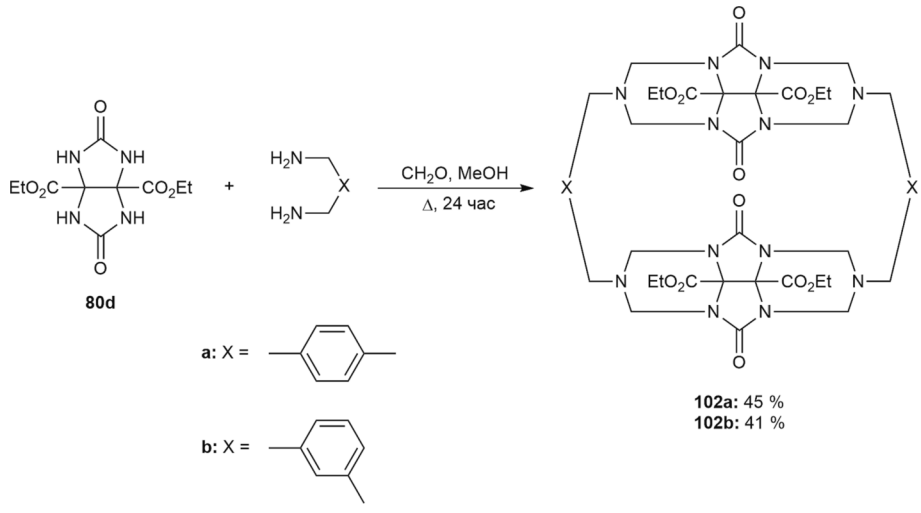


Fig. 4.4. Synthesis of macrocyclic polyamines.

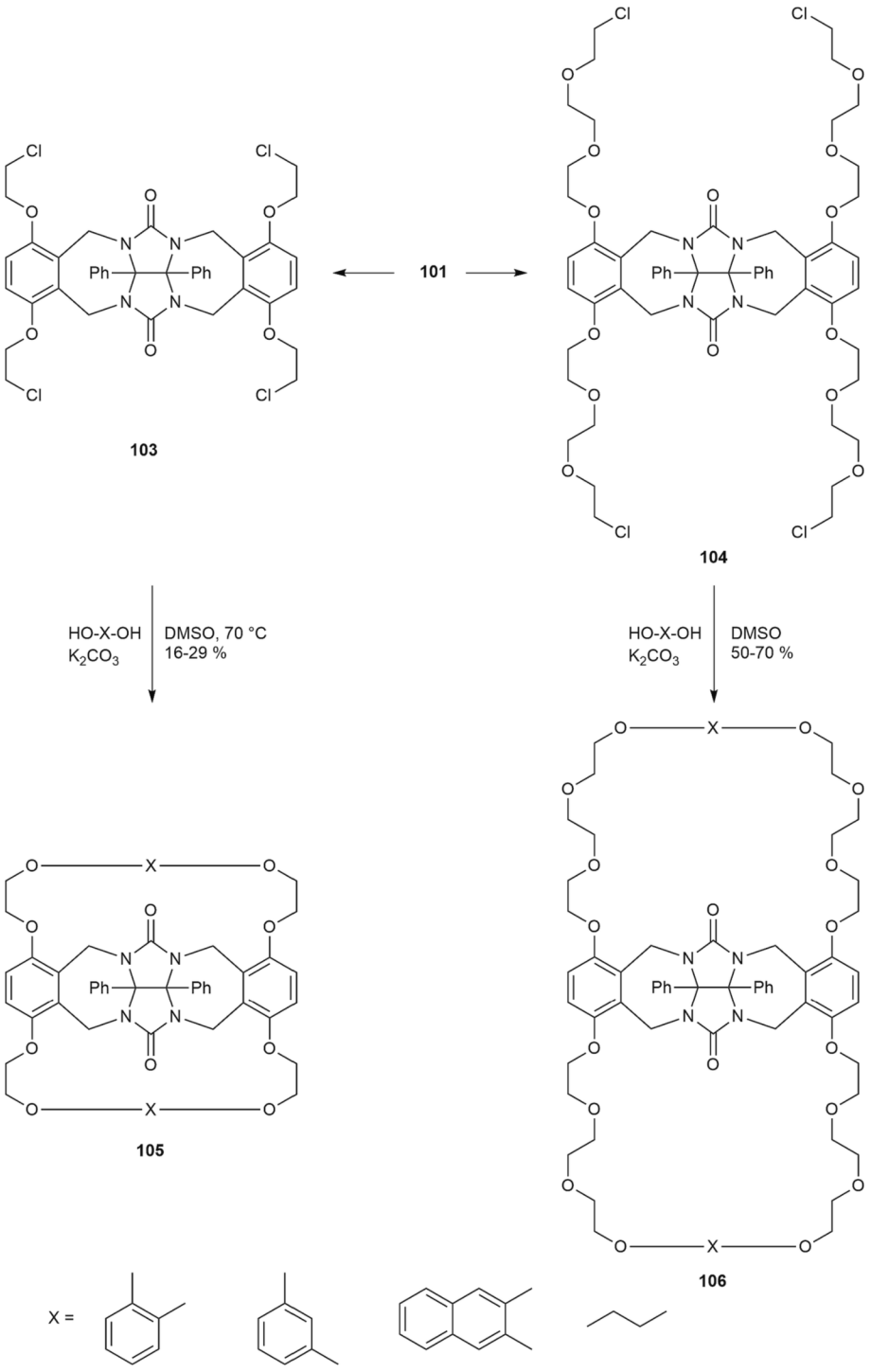


Fig. 4.5. Macrocycles from tetraphenol **101.**

Aminomethylated glycolurils in a strongly alkaline environment are decomposed through the N-CH_2 bond with the formation of the initial glycoluril, which is an argument for using named derivatives for aminogroup protection.

Compounds of general Formula **76** – effective stabilizers for natural and synthetic polymeric materials – are obtained through the reaction of glycoluril **1** with phenols and formaldehyde [102].

The reaction of 1,6-dimethylglycoluril **77** with piperidine and formaldehyde [103] gives di-*N*-piperidinemethylglycoluril **78** (Fig. 3.29).

For the synthesis of tetracyclic compounds **79a–v, a** three-component condensation of glycoluril **1** with formaldehyde and amines was used (Fig. 3.30). For example, this approach was used in the synthesis of three tetracyclic Compounds **79a**, **b**, **q**, and **v** through glycoluril **1** interaction with formaldehyde (4 mol) and 2 mol of the respective amine [96,104]. Tetracyclic Compound **79a** was synthesized with 33 % yield, but the conditions required for the reaction of glycoluril **1** with formaldehyde and methylamine are not given in this patent. For synthesis of the second tetracyclic Compound **79b**, according to this patent data with a yield of 80 %, the reaction mixture was heated for 2.5 h at 80 °C. The yield of Compound **79q** obtained in formamide was 52 %, and the yield of **79v** was 17 % [59].

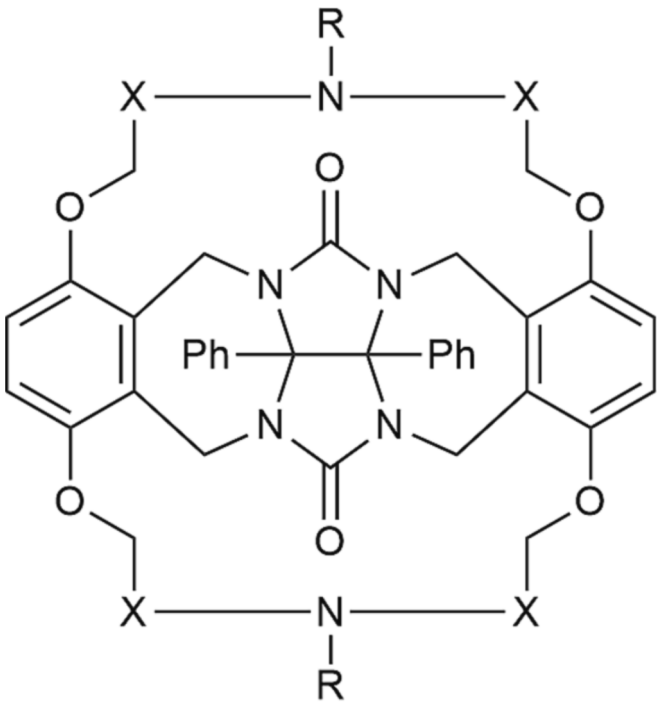


Fig. 4.6. Heterostructure **107.**

A new method of synthesizing Compounds **79b**, **e**, **l**, and **m** based on glycoluril **1** condensation with *N,N*-bis(methoxymethyl)alkylamines (R = Cy, *i*-Pr, *t*-Bu, $(CH_2)_2OH$) in a $CHCl_3$-EtOH environment using $SmCl_3{\cdot}6H_2O$ as the catalyst was suggested [59]. Desired products were separated using column chromatography, and the yield of Compounds **79b**, **e**, **l**, and **m** was 70–81 %.

Three-component condensation was used mainly for obtaining diethyl-2,6-dialkyl-4,8-dioxo-1,3,5,7-tetrahydro-1H,5H-2,3a,4a,6,7a,8a-hexaazacyclopenta[def]fluoren-3a 1,4-dicarboxylates **81a–j** through condensation of diethyl-2,5-dioxotetrahydroimidazo [4,5-d]imidazol-3a,6a (1H,4H)-dicarboxylate **80d** with 37 % formaldehyde water solution and alkyl-, aryl- or alkylarylamines (Fig. 3.31).

In addition, methods for obtaining Compounds **81a–j** were described; according to them, respective amine solutions in MeOH or MeCN were added dropwise to glycoluril and formaldehyde mixtures. In the case of using MeOH, amine solutions were added dropwise for 1 h, and the reaction mixture was boiled under reflux for 9–24 h. The yield of tetracyclic compounds obtained through this method ranged between 10 and 76 %. To increase tetracyclic compounds **81b–e**, acetonitrile was used as a solvent for amines, and the reaction mixture was mixed for 12 h at room temperature. This approach allowed us to obtain tetracyclic compounds **81b–e** and **81 h** in 90 % yield. Synthesis of tetracycles **81j** was performed in different solvents (MeOH, EtOH, THF, DMF) [95,105–117]. The authors found that the optimal conditions for diethoxycarbonylglycoluril **80d** reactions with formaldehyde and aromatic amines (aniline, p- toluidine, m- toluidine, p-methoxyaniline, p-isopropylaniline, p-chloroaniline, p-bromo-aniline, p-iodoaniline, p-ethynylaniline) are as follows: DMF was used as a solvent, and the reaction mixture was kept at 120 °C for 16 h, where the **81j** product yield was between 24 and 61 %.

When p-nitroaniline and p-aminopyridine were used in similar reactions, the expected tetracyclic compounds were not obtained. In another study, Compound **81j** (R_3 = Ph, p-Tol) was obtained with 70 % and 60 % yields, respectively, but the only recorded reaction parameter was its time (12 h).

Dicarboxylate **82** was obtained through condensation of dimethyl-2,5-dioxotetrahydroimidazo[4,5-d]imidazol-3a,6a(1H,4H)-dicarboxylate **80c**, paraformaldehyde and *tri*-butylamine in acetonitrile at room temperature.

Compound **83a** (yield 12 %) was obtained through condensation of 3a,6a-diphenylglycoluril **80b** with formaldehyde and ethylamine by boiling the initial substances in MeOH solution [118]. The synthesis of Compounds **83b–c** was also performed with 90 % yield in acetonitrile at room temperature [105,119].

Compound **84** was obtained through the reaction of 3a,6a-dimethylglycoluril **80a** with cyclohexylamine [120].

Synthesis of glycoluril tricyclic derivatives, 2a,2a1-disubstituted 6-alkyltetrahydro-5H-2,3,4a,6,7a-pentaazacyclopenta[cd]-indene-1,4-(2H,3H)-diones **85–87** was obtained through three-component condensation of 3a,6a-disubstituted tetrahydroimidazo[4,5-d] imidazol-2,5-(1H,3H)-diones **1**, **80b**, **80d** with formaldehyde (used in form of solutions in a respective solvent) and amines or amino acid potassium salts (Fig. 3.32) [90,105,111,121–124].

Reactions were performed in solutions of H_2O, MeOH, EtOH and MeCN. Tricyclic compounds **85a–c** were obtained with 35–50 % yield by reaction mixture conditioning for 2 h at 90 °C. The observed products were formed through oligomerization between *N*-(hydroxymethyl)-glycolurils with different rates of hydroxymethylation along nitrogen atoms as well as oligomerization of these compounds with amino acids.

Synthesis of Compound **87a** (yield 20 %) was performed in acetonitrile at room temperature for 12 h. To synthesize Compounds **87b–c,** the reaction mixture was boiled under reflux in MeOH. Compound **87d** was obtained similarly using EtOH instead of MeOH (reaction time 10–12 hrs.). The yields of products **87b–d** were within 45–80 %.

The condensation reaction between 3a,6a-diphenyltetrahydroimidazo[4,5-d]imidazol-2,5 (1H, 3H) dithione **88**, formaldehyde water solution (37 %) and (S)-2-aminopropane-1-ol afforded tricyclic compound **89** (Fig. 3.33), but the yield was not reported [125].

It should be noted that condensation between glycoluril **1**, formaldehyde and isopropylamine in acetonitrile at room temperature (Fig. 3.34) led to the formation of 2,3-bis(hydroxymethyl)-6-

Fig. 4.7. Synthesis of macrocyclic structure **109.**

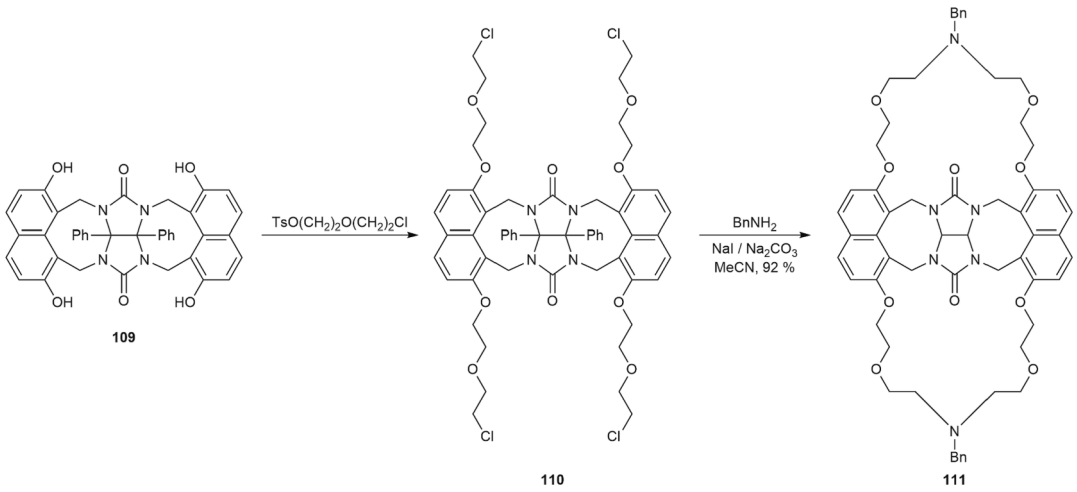


Fig. 4.8. Synthesis of macrocycles **110** and **111.**

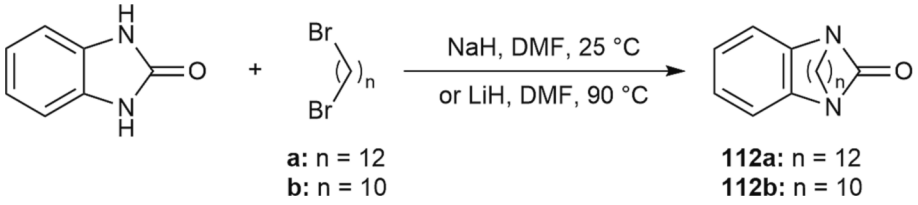


Fig. 4.9. Synthesis of macrocycles **112.**

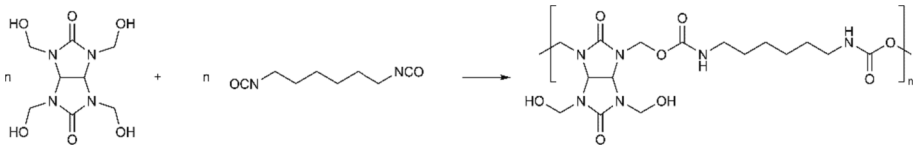


Fig. 4.10. Reaction of THMGU **29** with hexamethylenediisocyanate.

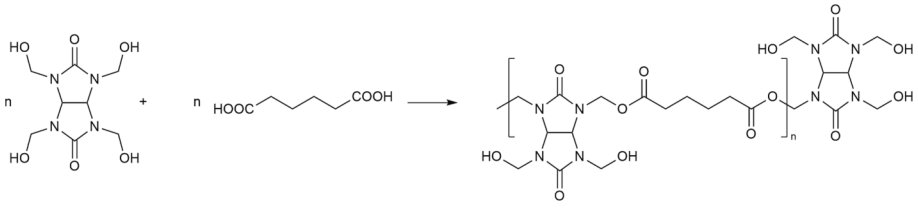


Fig. 4.11. Reaction of THMGU **29** with adipic acid.

isopropylhexahydro-1H-2,3,4a,6,7a-pentaazacyclopenta[cd]indene-1,4 (2H)-dione **90** with 20 % yield [126].

First, one-stage condensation reactions of 1-(*tert*-butyl)- or 1-cyclohexyltetrahydroimidazo[4,5-d]imidazol-2,5-(1*H*,3*H*)-diones **91a–b** by formaldehyde and aliphatic amines (Fig. 3.35) were performed [127]. As a result, 2-substituted 6-alkyltetrahydro-1H-2,3,4a,6,7a-pentaazacyclopenta[cd]indene-1,4 (2*H*,3*H*)-diones **93–94** with high yields within 70 and 84 % were obtained through the formation of intermediate Compounds **92a–b**.

5. Glycoluril macrocyclic derivative synthesis

Interest in macrocyclic polyamines is caused by the desire to obtain new objects for research in supramolecular chemistry characterized by the ability for self-assembly and molecular recognition.

Boiling tetra-*N*-hydroxymethylglycoluril **29** or its analogs in aqueous formaldehyde solutions with polymethylenediamines (tetra-*N*-pentamethylenediamines) leads to the formation of hexacyclic heterosystems **95** (Fig. 4.1) with different numbers of CH_2-groups in the side groups (2–5), where yields range between 54 % and 70 % [128].

Heating **29** or its derivatives with piperidine aminoalkyl derivatives gives macrocyclic polymer **100** (Fig. 4.2) with great light-stabilizing properties [94,129].

Condensation of tetra-*N*-hydroxymethyl-1,5-diphenylglycoluril **96** with hydroquinone (Fig. 4.3) gives polycyclic tetraphenol **101** [130], which forms complexes with hydroquinones [131] and is a semiproduct for the synthesis of new macrocyclic heterosystems [132].

Macrocyclic polyamines **102** were obtained through condensation of 6a-bis(ethoxycarbonyl)glycoluril **80d**, formaldehyde (37 % water solution) and aliphatic diamines with boiling under reflux for 24 h in MeOH

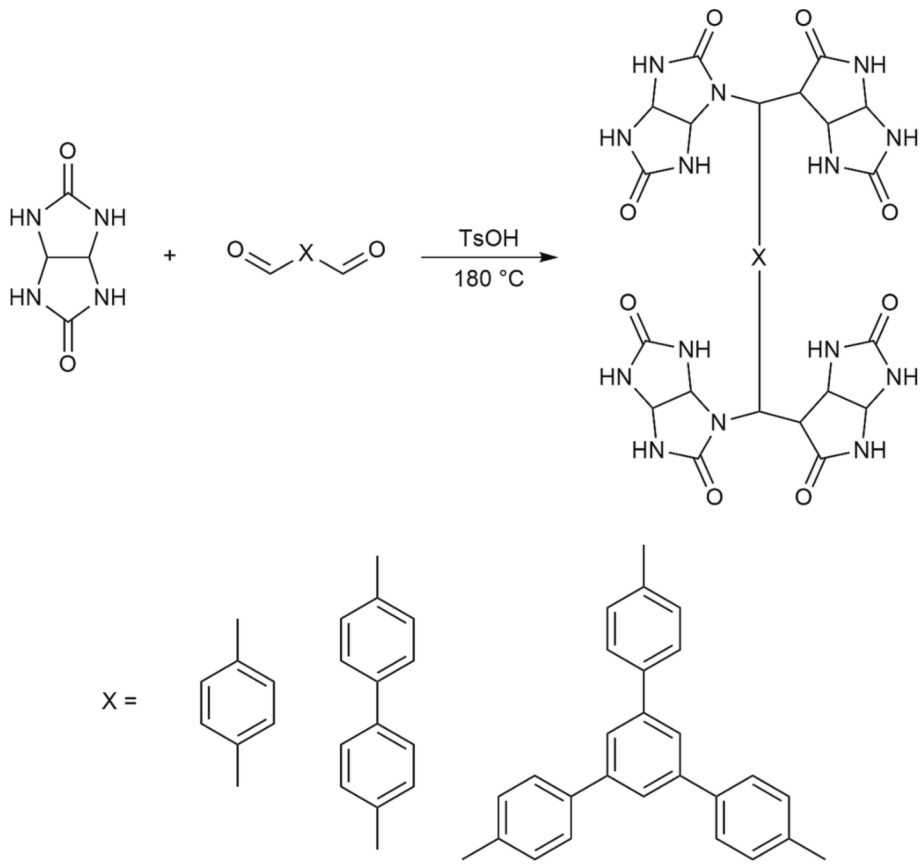


Fig. 4.12. Synthesis of polymers based on glycoluril and aromatic aldehydes.

(Fig. 4.4). The yields of products **102a–b** reached 45 and 41 %, respectively [105].

In this way, the interaction of tetraphenol **101** with 1-chloro-2-tosylethane or 1-(2-chloroethoxy)-2-tosylethane synthesizes respective products of tetra-O-alkylation **103–104,** which are further cyclized into DMSO in a basic environment in the presence of respective diols or diphenols [132] with the formation of products **105–106** (Fig. 4.5).

Compounds **105** and **106** form complexes with cations and dications (alkaline metals, NH_4^+, RNH_3^+, $^+H_3N(CH_2)_nNH_3^+$ (n = 3 9), xylylene- and phenylenediammonium) with a stoichiometry of 1:1. In the authors' opinion, the structure of these complexes is similar to a sandwich or a "clamshell". Strong complex formation with dihydroxybenzols is observed for **107**-type heterostructures (Fig. 4.6), which are synthesized through the interaction of compound **103** with respective amines [133].

Compound **107** contains a "gap" formed by a diphenylglycoluril fragment and two O-xylylene rings with an almost parallel orientation. Nitrogen atoms in azacrownether bridges are capable of forming hydrogen bonds with dihydroxybenzol hydroxylic groups. The binding constants of macrocycle **107** with isomeric dihydroxybenzols decrease in the following order: resorcinol > hydroquinone > catechin.

THMGU **29** under regular chlorinating reagents easily turns into tetra-*N*-chloromethylglycoluril **108**, cyclocondensation of which with 2,7-dihydroxynaphthalene (Fig. 4.7) leads to macrocycle **109** [134].

The result of the interaction of macrocycle **109** with $TsO(CH_2)_2O(CH_2)_2Cl$ in a superbasic environment in an inert atmosphere is tetra-O-alkyl derivative **110,** which in turn undergoes cyclocondensation with benzylamine, turning into Compound **111** (Fig. 4.8). Macrocycles **110** and **111** can form stable complexes with nitroaromatic compounds, such as nitrobenzene [135].

Cryptands, unlike crown ethers, are much stronger and more selective complex formers for alkaline metal ions. The most well-known cryptands are typically aminopolyethers, and adding carbamide groups into the polyether cycle significantly changes the complex-forming properties of coronands [136–141]. Originally, the synthesis of macrocyclic heterocycles **112** with carbamide groups was performed through the interaction of benzimidazol-2-one with α,ω-dibromalkanes in DMF (Fig. 4.9) in the presence of sodium hydride at 25 °C or lithium at 90 °C[136].

Generally, references analysis shows that synthetic research aimed at obtaining condensed tri-, tetra-, poly- and macrocyclic polyamines through combining easily accessible reagents (glycolurils, formaldehyde and amines or amino acids as well as polyamines) are rather modern studies. Continuous progress in this area is caused by the practical importance of these compounds and their application in supramolecular chemistry research.

As discussed above, data on glycoluril-based polymers of the non"-cucurbituryl" type are scarce in references.

Polyurethane prepolymers were synthesized through the interaction of THMGU **29** with hexamethylenediisocyanate in a mixture of chlorobenzene and o-dichlorobenzene (Fig. 4.10). The average molecular mass of the obtained prepolymers is 1800 [142].

The authors also performed step-by-step polymerization of THMGU with adipic acid (Fig. 4.11). As a result, a mixture of polytetra-*N*-hydroxymethylglycoluriladipinate oligomers was obtained with an average molecular mass of 2860.Fig. 4.12.

Polyether was added to the reaction with diisocyanate under vacuum to avoid frothing. The obtained polyether urethane is a solid wax-like product with a molecular mass of 4310 that is poorly dissolved in organic solvents.

The creation of porous glycoluril-based materials through the reaction of glycoluril with different aldehydes at high temperatures in the presence of an acidic catalyst was reported [143]. A mixture of aldehyde, glycoluril and p-toluene sulfonic acid was mixed in a test tube and degassed through freezing and thawing cycles. Then, the tube was

frozen at 77 K, vacuumed, heated to 180 °C and conditioned at this temperature for 24 h. The obtained polymer was washed with organic solvents and dried under vacuum for 12 h. The authors used terephthaldehyde, 4,4-diphenylcarboxyaldehyde and 1,3,5-tris(4-formylphenyl)benzenealdehyde.

Polymers synthesized in this way have developed a specific surface area of up to 1010 m^2/g and the ability to absorb gases, which makes them promising materials for gas storage and separation.

6. Conclusion

In conclusion, it is necessary to turn researchers' attention to the following points in tracking the synthesis of new glycoluril-based macrocyclic compounds:

Glycoluril is not a perfect model for the biomimetical cycle, first due to its low solubility in most organic solvents, which often leads to very strict conditions for the direct synthesis of desired macrocyclic compounds. One of the interesting possibilities for overcoming this obstacle is using other glycoluril derivatives by adding a reagent to the parent glycoluril model or (more efficiently) to its reactive adduct, which generally leads to different interesting unexpected structures.

Glycoluril model design in macrocyclic compound synthesis is mostly based on condensation reactions and is rarely presented by some other reactions.

In addition, based on the created summary, it can be said that the use of glycoluril in the synthesis of high-molecular-weight compounds (polymers) is relatively understudied and has enough unrevealed potential for performing a wide range of new research to obtain practically valuable substances.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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