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USE OF THE RING OPENING REACTIONS OF 1,3,5-TRIAZINES IN ORGANIC SYNTHESIS (REVIEW)*

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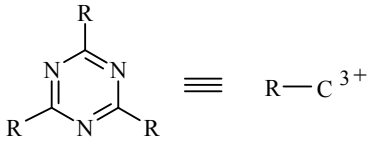
Published data on the recyclization reactions of 1,3,5-triazines are reviewed. The classification is based on the fragments of the 1,3,5-triazine molecules used in the construction of new heterocycles.

Keywords: azapyrenes, amidines, imidazoles, oxazoles, perimidines, pyridines, pyrimidines, thiazoles, 1,3,5-triazines, *peri* annelation, acylation, heterocyclization, recyclization, formylation.

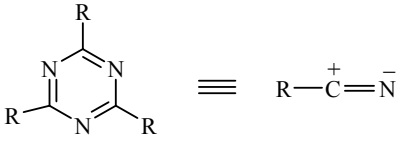
It is well known that 1,3,5-triazine undergoes ring opening under the influence of various nucleophilic reagents by acting as a precursor of a formyl group. This property has determined its use in organic chemistry. It is to such reactions that this review is directed.

Theoretically, 1,3,5-triazines can act as a source of:

1) –CR=, here the carbon atom of the triazine is used in the construction of new molecules



2) –CR=N–, the carbon and nitrogen atoms are used



* Dedicated to the birthday of A. F. Pozharskii, who has made a great contribution to our establishment as scientists.

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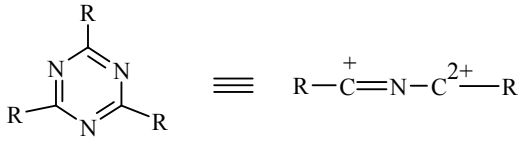
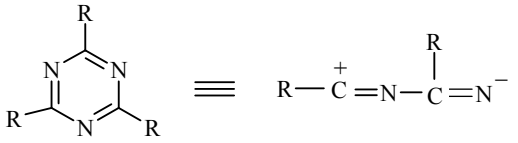
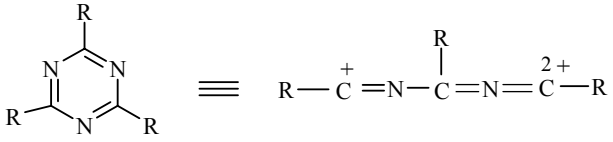
3) –CR=N–CR=, two carbon atoms and one nitrogen atom are used



4) –CR=N–CR=N–, two carbon atoms and two nitrogen atoms are used



5) –CR=N–CR=N–CR=, three carbon atoms and two nitrogen atoms are used

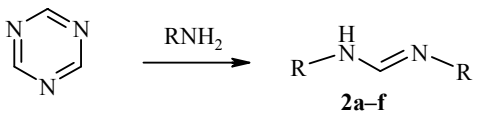


Strictly speaking, all known reactions of 1,3,5-triazines with nucleophilic reagents that take place with ring opening are among the presented cases. We will consider them in order.

1. Reactions in which the 1,3,5-Triazines are the Source of the Carbon Atom

Such reactions correspond to the first case. They take place in a fairly simple way. In the case of monofunctional nucleophilic reagents one molecule of the nucleophilic reagent (the 1,3,5-triazines are the source of −CR=N−) – this is from a different Section – or two molecules (–CR=) can take part in the reaction, and in the latter case they can be two molecules of one and the same reagent or of different reagents. With binucleophiles the result depends on the mutual arrangement of the nucleophilic centers. In the case of 1,4- and 1,5-binucleophiles and also, with a small yield, 1,6-binucleophiles heterocyclization takes place with closure of a five-, six-, or seven-membered ring [1]. With 1,7-binucleophiles and so forth polymers are formed [2]. Amines, ammonia and amides, hydroxylamine, compounds with an active methylene group, aromatic substrates, etc. can act as nucleophiles.

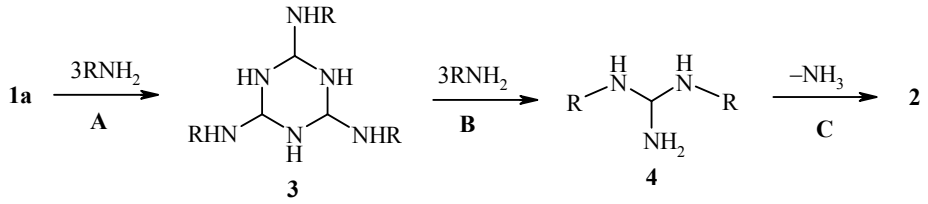
The reaction of 1,3,5-triazine **1a** with amines usually takes place with opening of the triazine ring and the formation of the corresponding amidines **2** [1, 3-6].



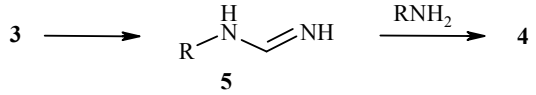
1a **2a–f**

2 a R = Bu, **b** R = $Me(CH_2)_6$, **c** R = $Me(CH_2)_{11}$, **d** R = Ph, **e** R = $PhCH_2$, **f** R = C_6H_{11}

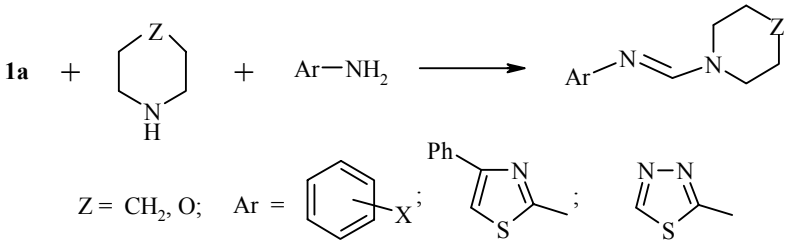
The yield is close to quantitative (84-100%) [1]. With substituted triazines, as also with secondary amines, the reaction does not occur [1]. The authors proposed the following reaction mechanism [1]:



In this mechanism there is some doubt about stage **B**. It seems more likely that the monosubstituted amidine **5** is formed initially and that compound **4** is formed from it.

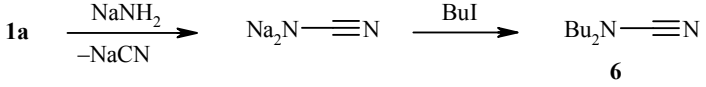


In [4-6] it was demonstrated that two different amines, primary and secondary, can be used in this reaction.

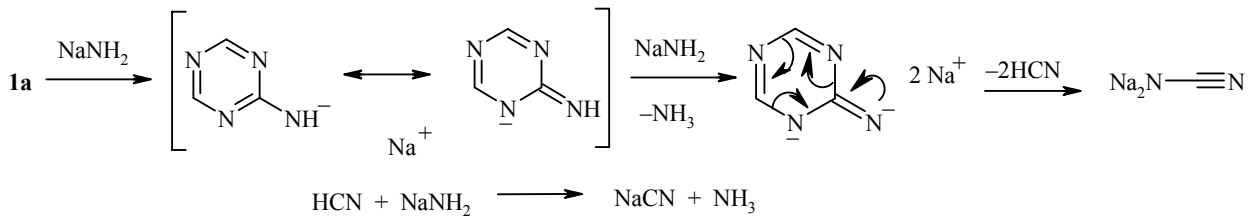


The reaction with ammonia takes place similarly [20], but the product decomposes on account of its instability in the form of the free base at temperatures above 100°C. If an ammonium salt is used in place of ammonia the yield of formamidine hydrochloride is close to quantitative [7].

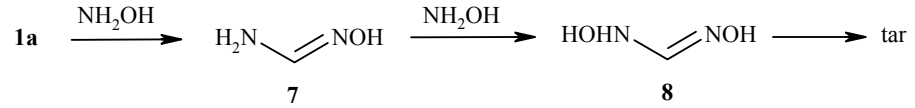
1,3,5-Triazine reacts with sodium amide in xylene at 160°C (autoclave), forming the disodium salt of cyanamide, and this was confirmed by its transformation into dibutylcyanamide **6** [8].



The authors proposed a completely implausible mechanism [8], involving the reaction of sodium cyanide with sodium amide. In our opinion the reaction takes place in the following way:



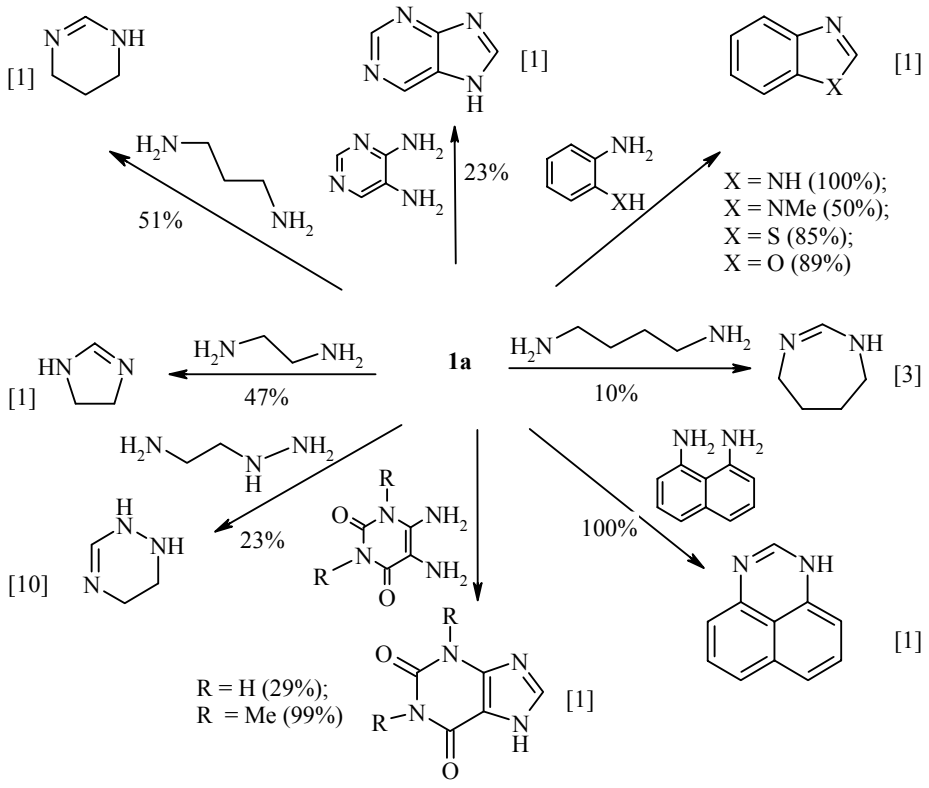
The reaction of the triazine **1a** with hydroxylamine takes place similarly to the reaction with ammonia.



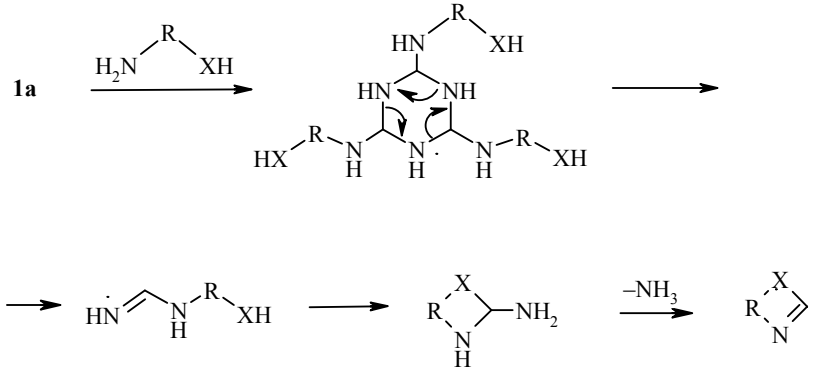
7 **8**

In this case, as also with ammonia, the yield of compound **7** is low (13%). Strong tarring is observed, and this is explained by the instability of the compound **8** that is probably formed during the reaction [9].

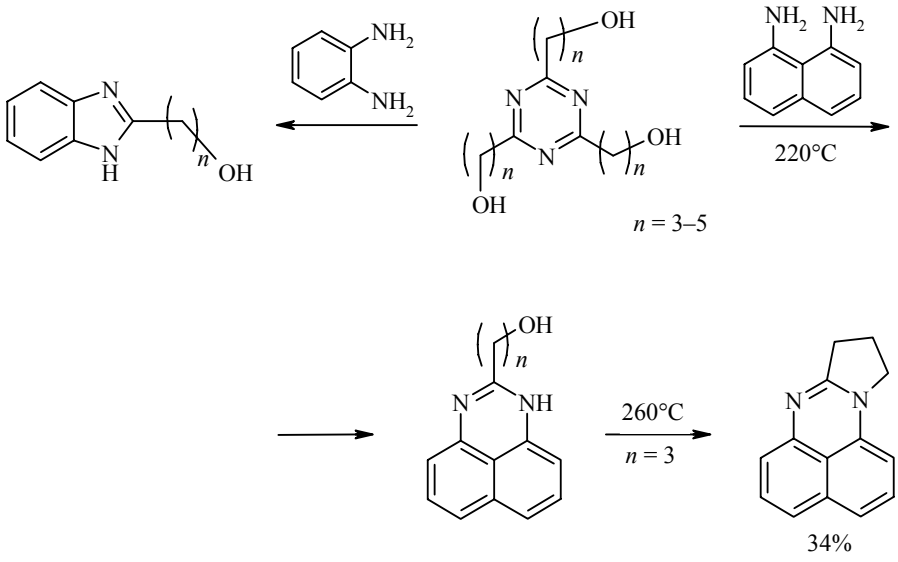
As mentioned above, heterocyclization occurs with diamines and amines containing a nucleophilic center at positions 4, 5, or 6 in relation to the amino group [1, 3, 10, 11].



All the transformations probably take place according to the following mechanism:

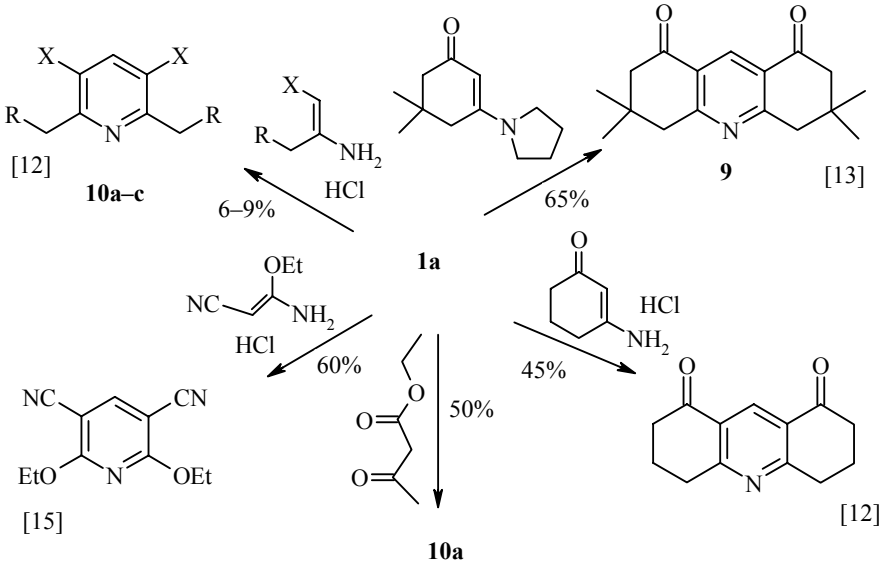


There are examples of similar reactions involving a substituted 1,3,5-triazine [11].



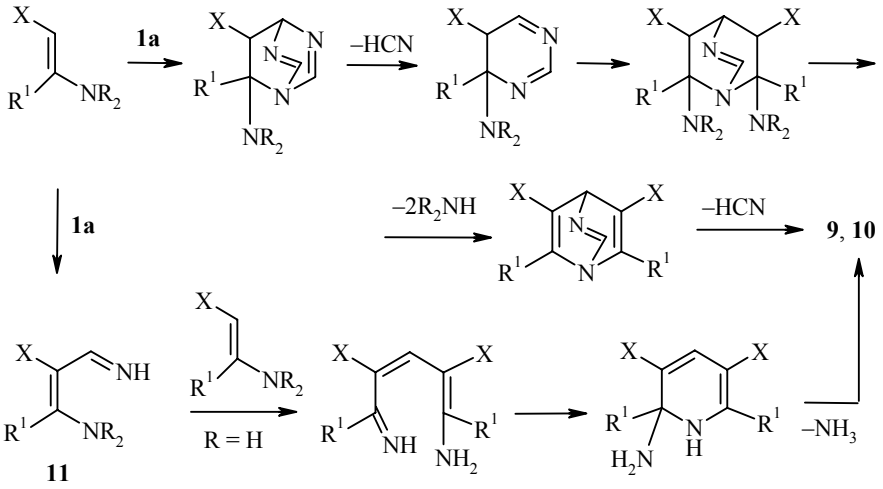
In the case of 1,8-naphthylenediamine a secondary cyclization product was obtained with a yield of 34% [11].

1,3,5-Triazine reacts fairly readily with C-nucleophiles. In this case two molecules of one nucleophile can also take part in the reaction, or the reaction can take place with two different nucleophiles in succession. As an example of a reaction of the first type it is possible to quote the formation of pyridines **9** from enaminones [12, 13], acetoacetic ester, and similar compounds [14, 15].

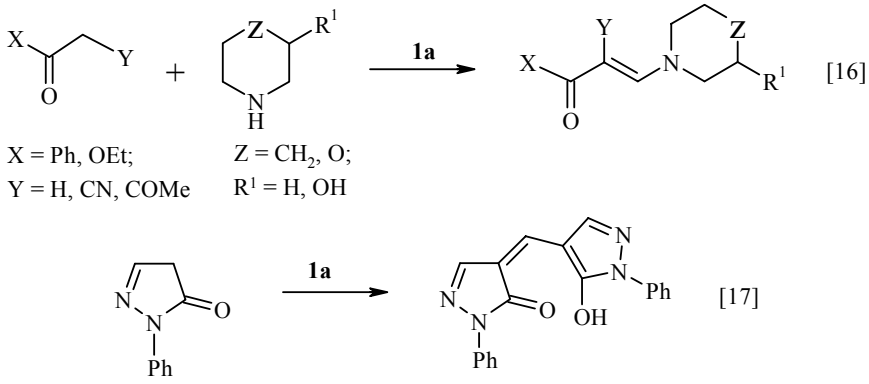


10 a R = H, X = CO_2Et; **b** R = H, X = COMe; **c** R = Me, X = CO_2Et

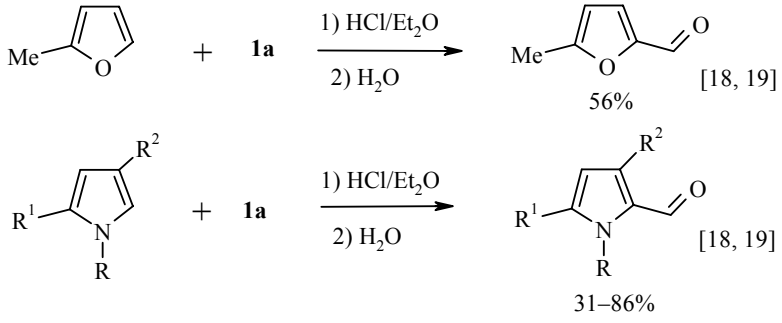
The corresponding pyrimidine is formed as second reaction product (see Section 2). The ratio and the yield depend on the solvent. The highest yield of the pyridine **9** (65%) is obtained in water [13]. The authors of [13] consider that its formation results from two successive cycloaddition reactions, whereas evidence both for cycloaddition and for a stage mechanism is discussed in [12].



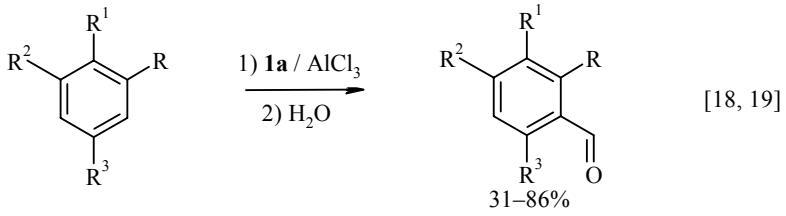
A stage mechanism is favored by results presented in [16, 17]. The authors of [16] were able to stop the reaction at the formation of compounds **11** by introducing an additional nucleophile (a secondary amine) into the reaction having realized a Mannich reaction with the triazine **1a**, while the authors of [17] were able to isolate the product from condensation with two molecules of a carbonyl compound.



Another example of such reactions is provided by the formylation of various aromatic compounds [18-23].

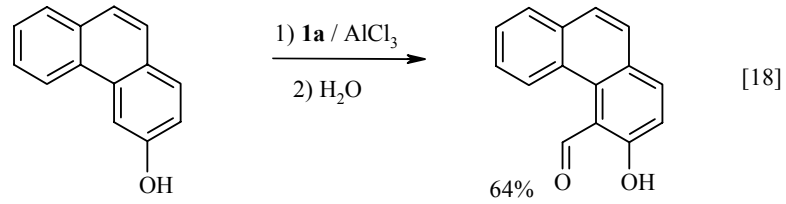


R = H, Me, Bu; R^1 = H, Me; R^2 = H, Me

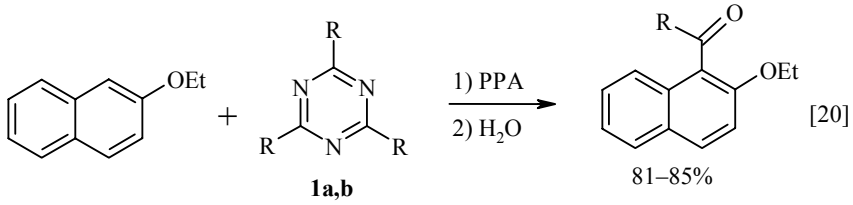


[18, 19]

R = H, OH; R^1 = H, OH; R^2 = H, OH, OMe, OPh; R^3 = H, OH, Me

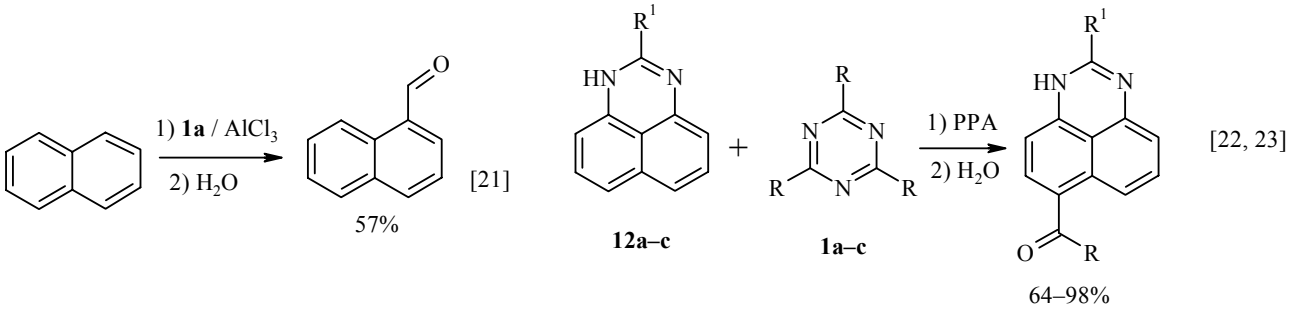


[18]



[20]

1a,b



[21]

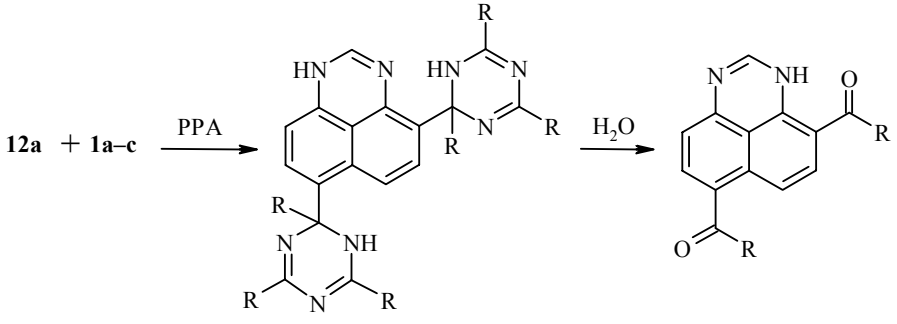
12a–c

1a–c

[22, 23]

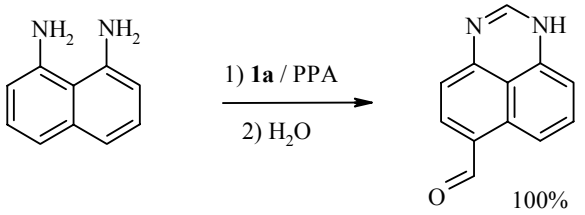
1, 12 a R = H, **b** R = Me, **c** R = Ph

Dry HCl [18], Lewis acids [18, 21], and polyphosphoric acid (PPA) [20, 22, 23] were used as catalysts. With active aromatic compounds the reaction takes place without a catalyst [18]. If an excess of the 1,3,5-triazines is used in polyphosphoric acid the perimidine **12a** is diacylated in different rings of the naphthalene system [24]:

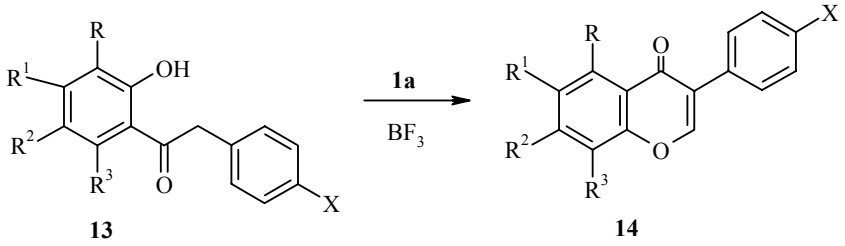


Such regioselectivity is explained by steric factors.

Heterocyclization with the formylation of 1,8-naphthylenediamine was reported in [25] during the use of an excess of the triazine **1a** in polyphosphoric acid.



If there is a second nucleophilic center in the molecule, as in the case of functionalized amines, ring closure occurs [26-28]. Thus, the reaction of 1,3,5-triazine with ketones **13** in the presence of boron trifluoride etherate leads to isoflavones **14** [26].

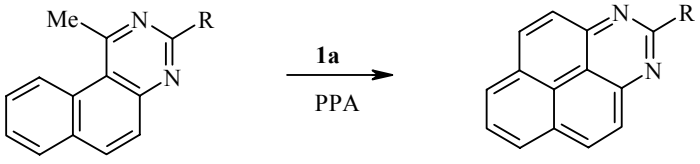


13 **14**

X = OH, OMe; R = H, OMe; R^1 = OH, OMe; R^2 = H, OH, OMe; R^3 = H, OH

In this reaction the role of second nucleophile is played by the hydroxyl group attached to the aromatic ring.

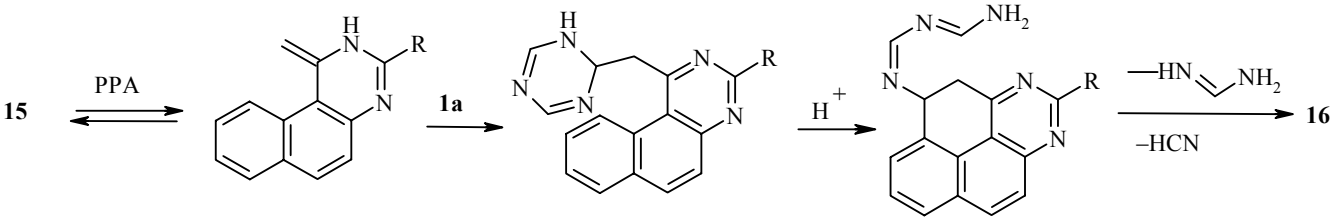
An aromatic ring can act as second nucleophile. For example, the reaction of 1,3,5-triazine with 1-methylbenzo[*f*]quinazolines **15** in polyphosphoric acid leads to 1,3-diazapyrenes **16** with yields of 22-31% [27].



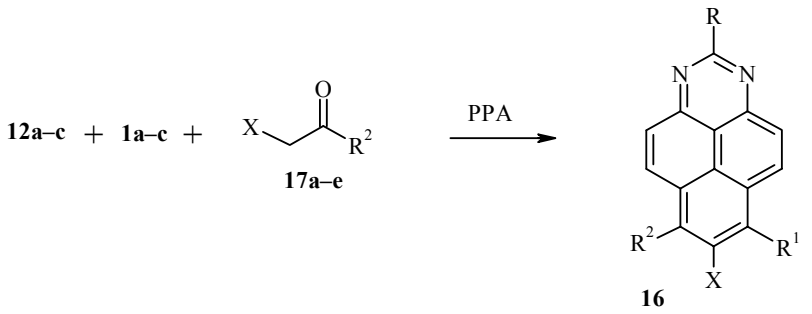
15a–c **16a–c**

15, 16 a R = H, **b** R = Me, **c** R = Ph

The authors postulate the following mechanism:

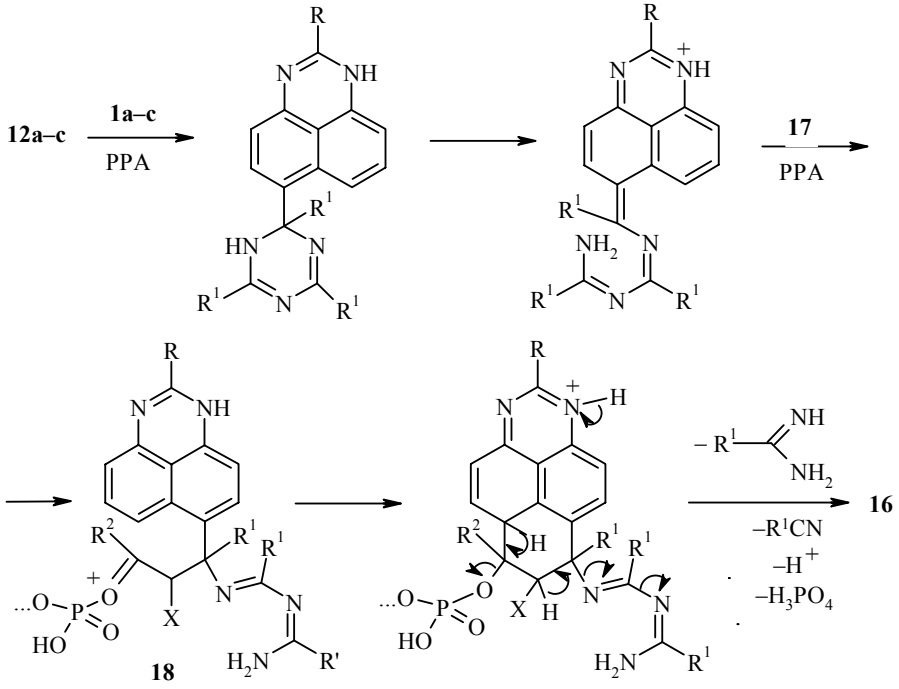


The second nucleophile in such reactions can then enter into various reactions. For example, the reaction of perimidines **12** with triazines **1** in polyphosphoric acid in the presence of ketones leads to good yields (37-75%) of 1,3-diazapyrenes **16** [28].

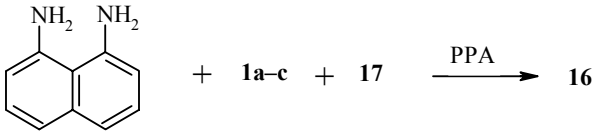


R = H, Me, Ph; R^1 = H, Me, Ph; R^2 = Me, Ph; X = H, CO_2Et, COMe

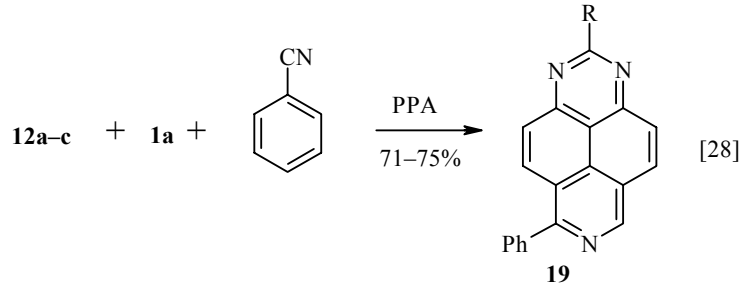
In this case the intermediate compound **18**, formed after reaction with the carbonyl compound, enters into intramolecular electrophilic substitution.

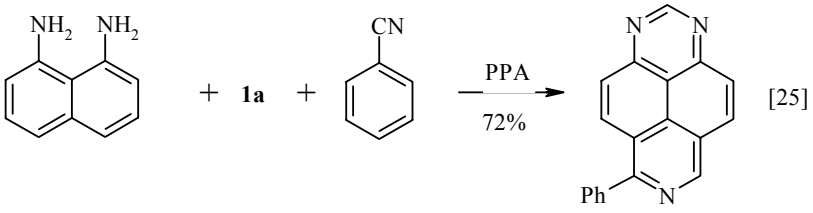


This reaction can be combined with heterocyclization [25].



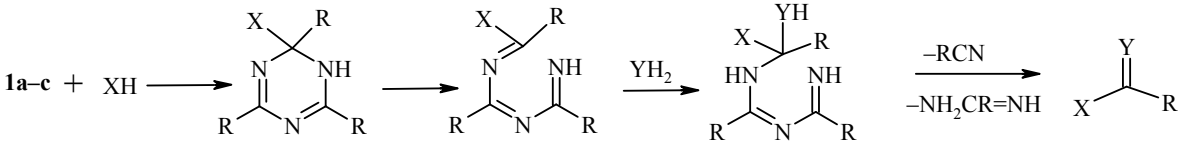
Another example of a similar transformation is the reaction of perimidines **12** [28] and 1,8-naphthylenediamine [25] with triazine **1a** in the presence of benzonitrile.





In these cases a second nucleophilic center is formed as a result of electrophilic substitution.

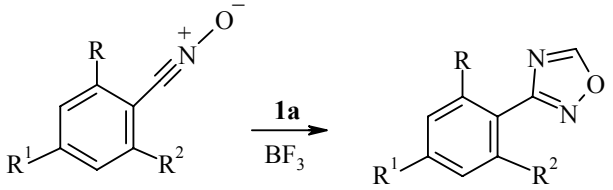
Thus, the reactions examined in this section take place according to the following general mechanism:



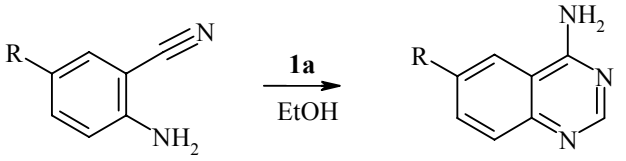
Subsequent transformations depend on the nature of X and Y. These nucleophilic reagents can be part of different molecules or of one molecule. In the latter case they may be 1,4-, 1,5-, or 1,6-binucleophiles.

2. Reactions in which 1,3,5-Triazine is the Source of the –CR=N– Fragment

Such reactions are realized in the presence of an electrophilic center at position 3 or 4 in relation to the nucleophilic center. In the first case the reaction represents 1,3-dipolar cycloaddition, where the triazine **1a** acts as dipolarophile. An example of such a transformation is the synthesis of 1,2,4-oxadiazoles from nitrile oxides [29].



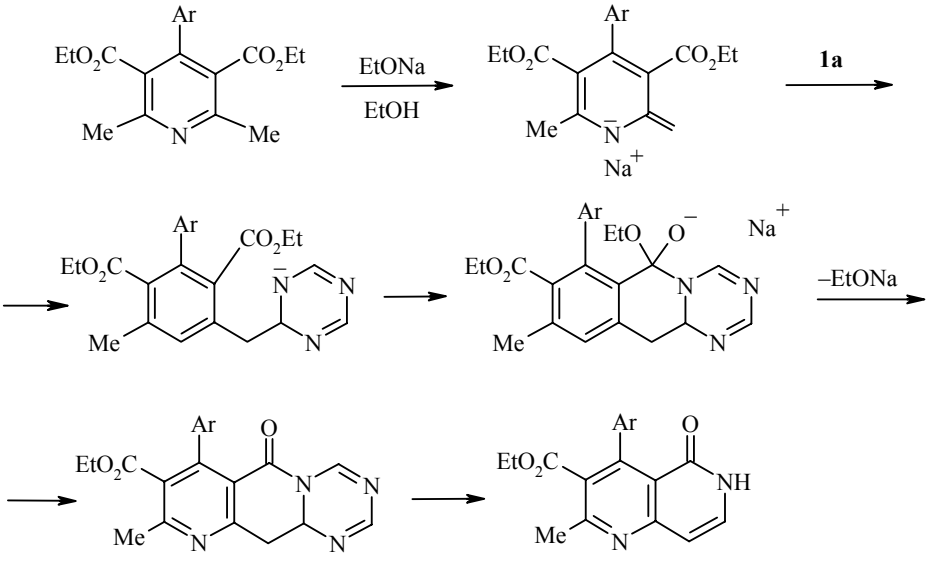
Examples of the closure of a six-membered ring were published in [4, 30-35]. Historically one of the first papers based on the transformation under discussion is the synthesis of 4-aminoquinazolines from the nitriles of anthranilic acids [4].



7–65%

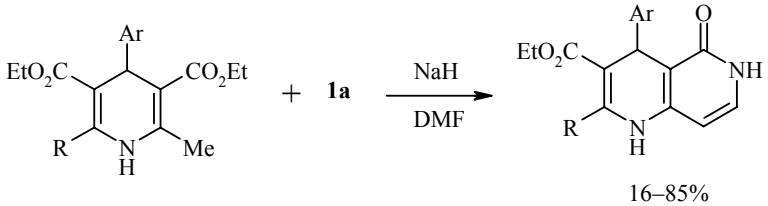
R = H, Me, Br

This example illustrates the use of an N-nucleophile. There are a number of examples involving C-nucleophiles [30-33]. In these cases the pyridine ring is annulated [30, 31].



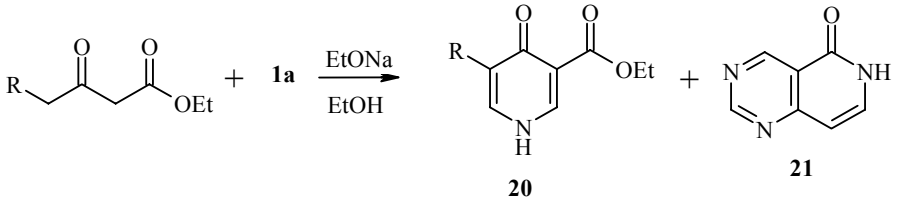
21–91%

The reaction with Hantsch pyridines takes place similarly, but in this case a stronger base is needed [32].



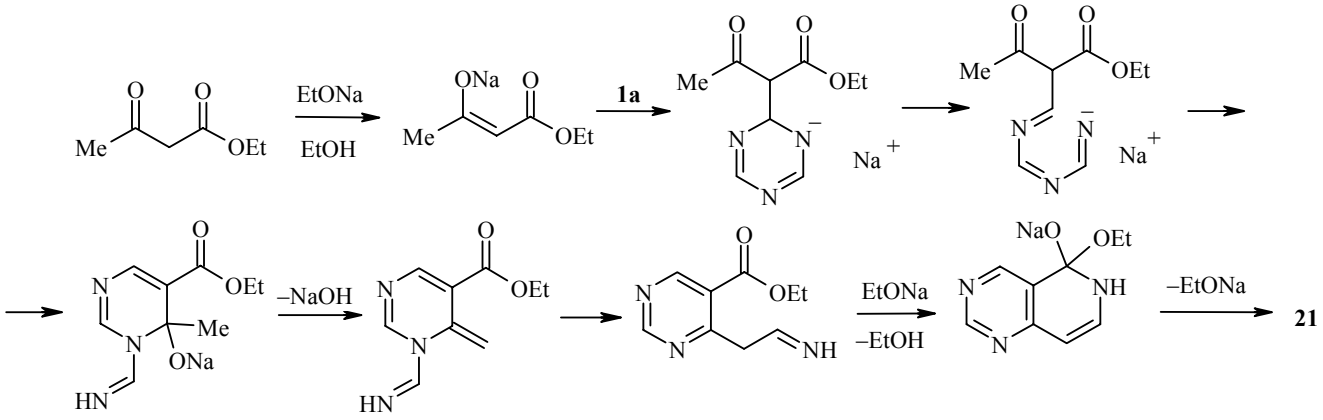
16–85%

The formation of compound **21** as side product (yield 12%) during the synthesis of 4-pyridones **20** by the successive closure of two rings (pyrimidine and pyridine) was reported in [33].



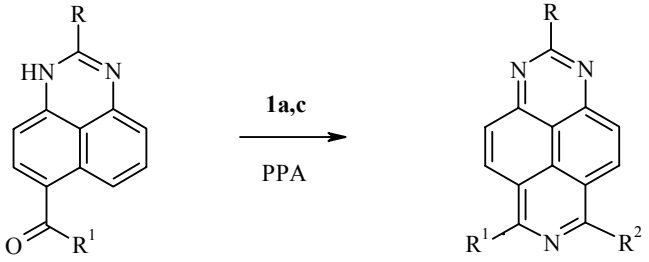
20 **21**

Compound **21** is probably formed by a scheme that includes nucleophilic addition of the dicarbonyl compound to the triazine and opening of the dihydrotriazine ring as key stages.

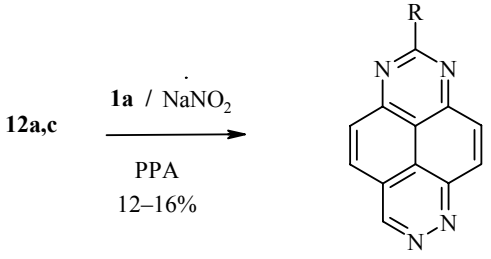


The mechanism of the formation the dihydropyridine **20** will be discussed below.

An aromatic ring can act as nucleophile. For example, the reaction of perimidines containing a carbonyl group at the *peri* position leads to annulation of the pyridine ring [34].



The examples presented above involved the participation of C-electrophiles. There is an example of the use of an N-electrophile. This is the three-component reaction of the perimidines **12** with the triazine **1a** in the presence of sodium nitrite [35].



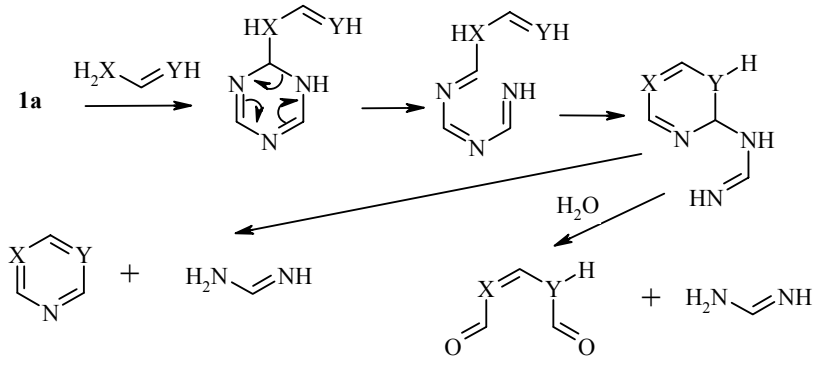
22 a R = H, **b** R = Ph

Unfortunately, the tetraazapyrenes **22** were produced with low yields.

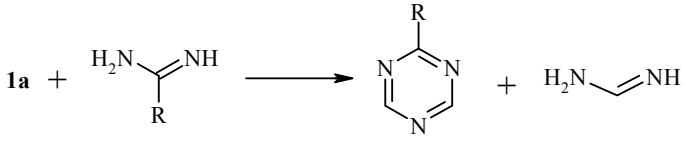
3. Reactions of 1,3,5-Triazines with Hydrazines and 1,3-Binucleophiles

Reactions of this type are similar to those discussed in Section 1. They occur when attack by the second nucleophile at the same atom as the first is unfavorable. In such reactions the 1,3,5-triazines act as source of the

–CR=N–CR= fragment, i.e., two azaformyl or two formyl (acetyl) groups, if this fragment is opened as a result of hydrolysis. If the initial compound is a binucleophile a six-membered ring is closed or a 1,5-dicarbonyl compound is formed. In general form the mechanism of these transformations looks as follows:

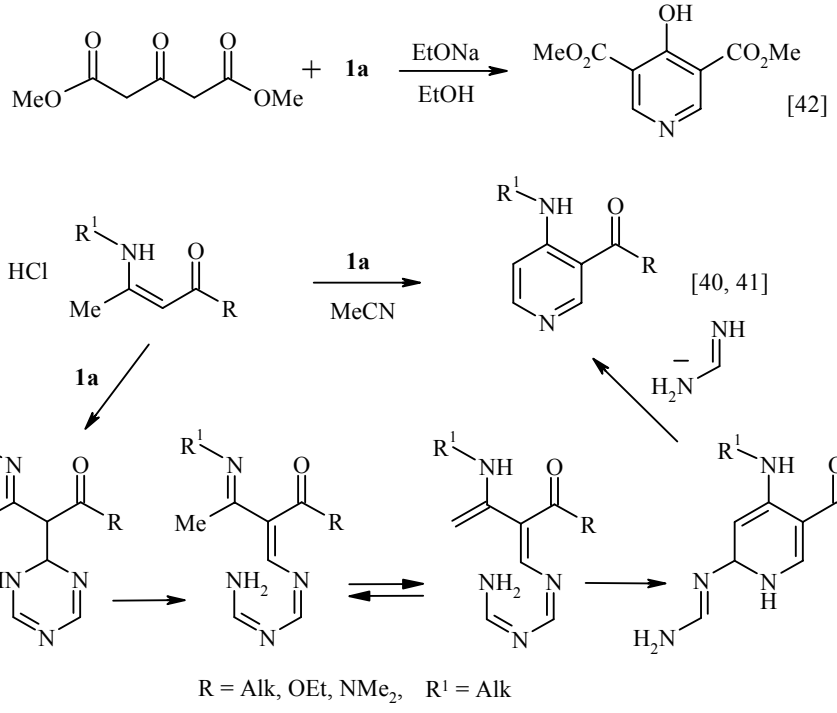


The simplest example of a reaction taking place according to this scheme is the reaction of 1,3,5-triazine with amidines X = Y = N [36-39].



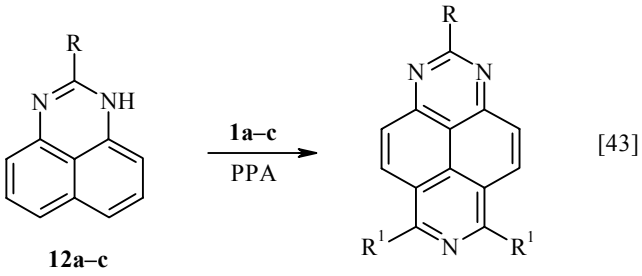
Substituted triazines are formed as a result of the reaction.

A series of examples of the use of 1,3-C-binucleophiles in reactions with 1,3,5-triazines have been described. In them, as mentioned above, a new pyridine ring is created. The pyridines [40-42] can be synthesized under conditions of base [42] or acid [40, 41] catalysis.

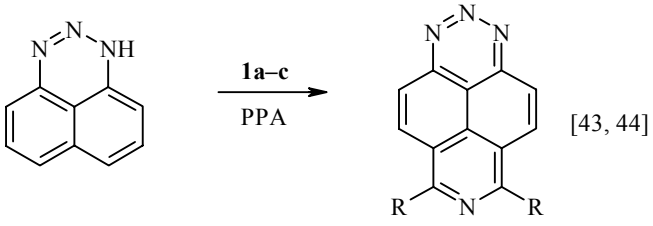


R = Alk, OEt, NMe_2, R^1 = Alk

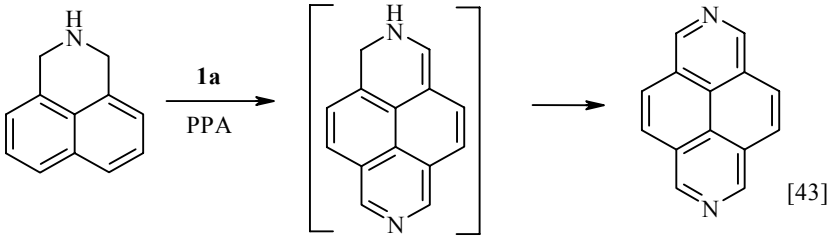
The *peri* positions of naphthalene systems can act as 1,3-binucleophiles. In this case *peri* annelation of the [*c*,*d*]pyridine ring occurs [43, 44].



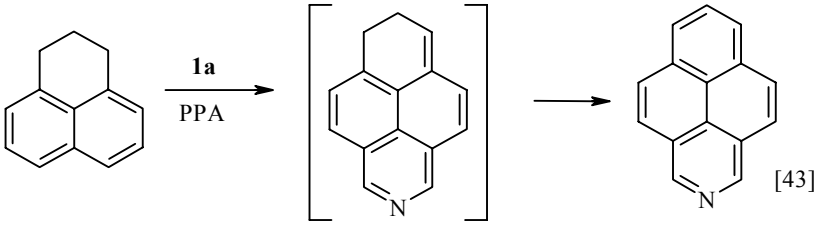
12a–c [43]



[43, 44]



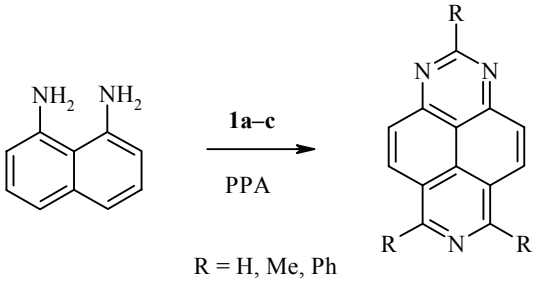
[43]



[43]

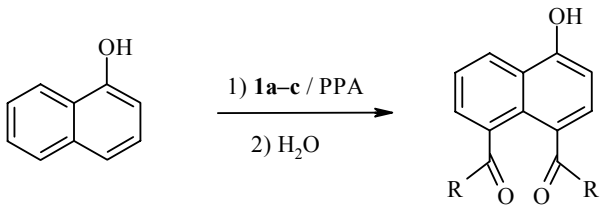
Azaphenalenes and their dihydro derivatives can be used as starting compounds. In the case of the latter the intermediate dihydro derivatives of azapyrenes are dehydrogenated spontaneously in the course of the reaction [43].

An example of the simultaneous closure of two rings in 1,3,7-triazapyrene was described in [45].



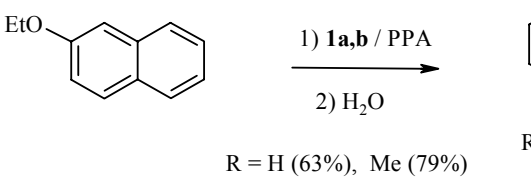
R = H, Me, Ph

With other derivatives of naphthalene and with naphthols and their ethers the reaction takes place rather differently. Regioselective 1,8-diacylation (formylation) occurs [20, 46]. A second variant of the mechanism presented at the beginning of this section is realized.



[46]

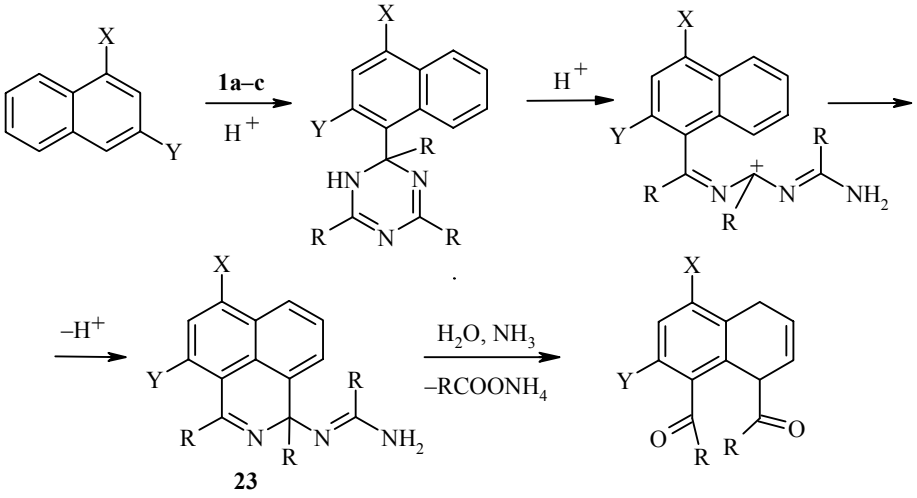
R = H (29%), Me (36%), Ph (54%)



[20]

R = H (63%), Me (79%)

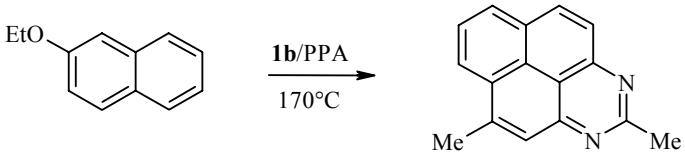
In this case removal of the amidine does not lead to a fully aromatic system, and hydrolysis with the formation of two carbonyl groups therefore occurs when the reaction mixture is treated with water.



23

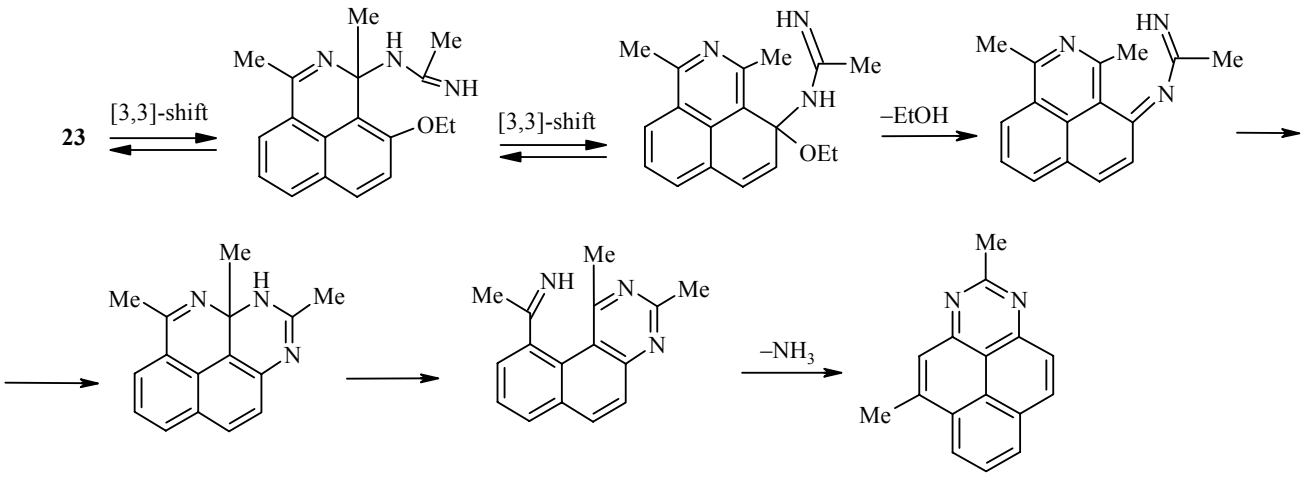
X = H, OH; Y = H, OEt; R = H, Me, Ph

An example of such a transformation was described in [47], but the amidine is not released during hydrolysis but takes part in the closure of an additional ring.

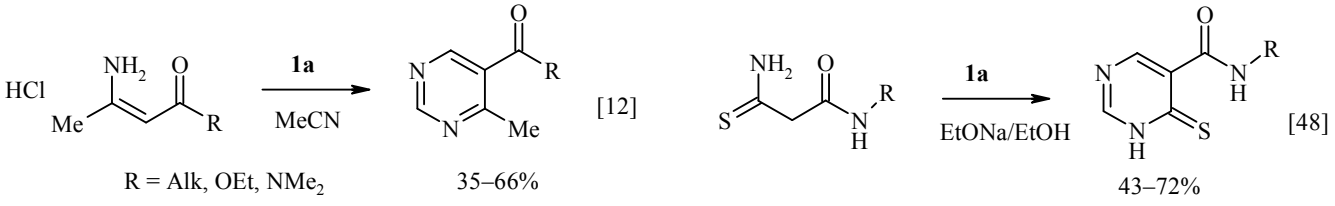


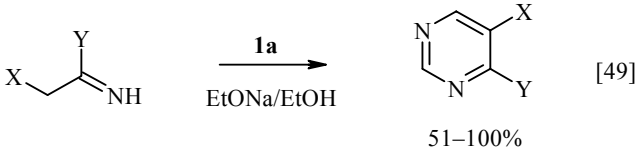
42%

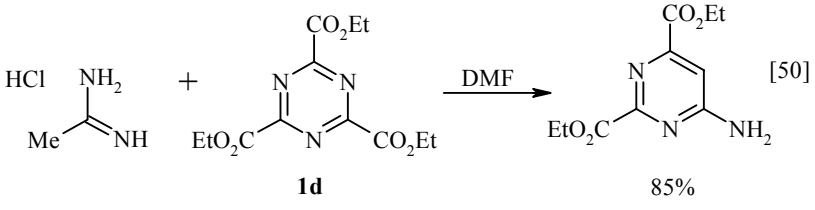
The authors postulate the following mechanism, involving the formation of the intermediate amidine **23**, as shown above:



The reactions of the triazines **1a**,**d** with 1,3-N,C-binucleophiles have also been studied quite well. They lead to the closure of a pyrimidine ring. Amidines, enamines, and thioamides can act as such nucleophiles [12, 13, 48-50].

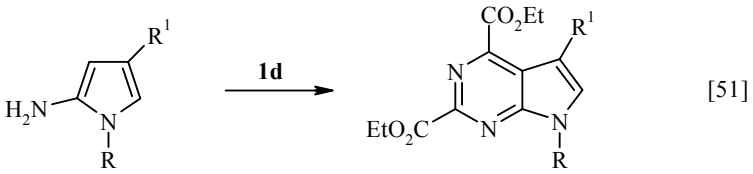




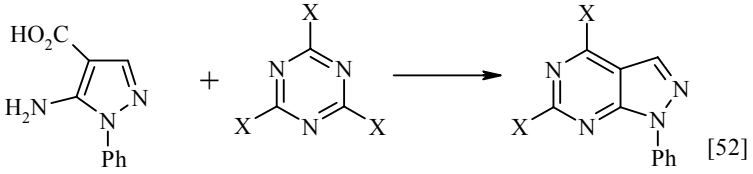


The authors of [50] consider that the reaction takes place as cycloaddition although, in our opinion, the stage mechanism favored by the data obtained in [12] is more likely.

There are a number of examples of such transformations where the C-nucleophilic center is a carbon atom of a five-membered heterocyclic system: pyrazole [51-53], imidazole [54], pyrrole [51].

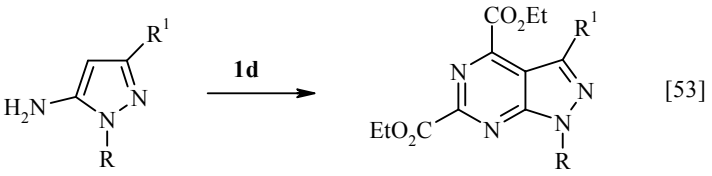


[51]

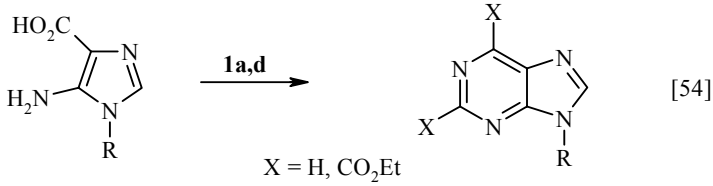


[52]

X = CO_2R, CF_3, $CClF_2$, H, Ph, MeS



[53]

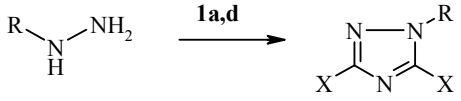


[54]

X = H, CO_2Et

The authors of these papers also postulate a synchronous mechanism although we consider that here is obviously a stage mechanism.

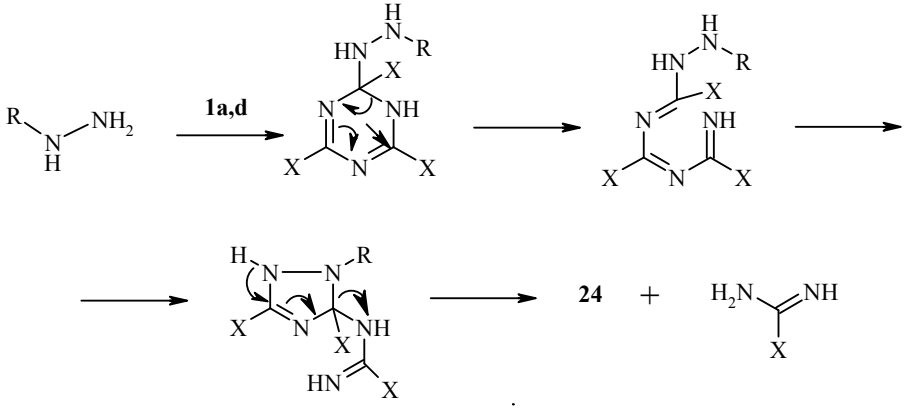
As a rule the reactions of the 1,3,5-triazines **1** with hydrazines take place similarly to the reactions with 1,3-bifunctional nucleophiles. 1,2,4-Triazoles are formed as a result [7, 55, 56].



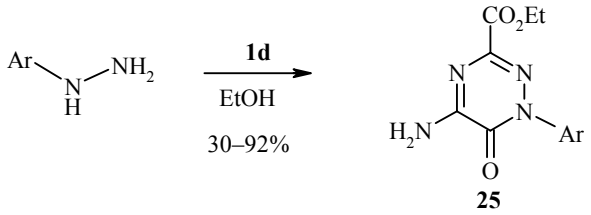
X = H, CO_2Et

24

The mechanism of this reaction is also similar to the mechanism presented at the beginning of this Section:

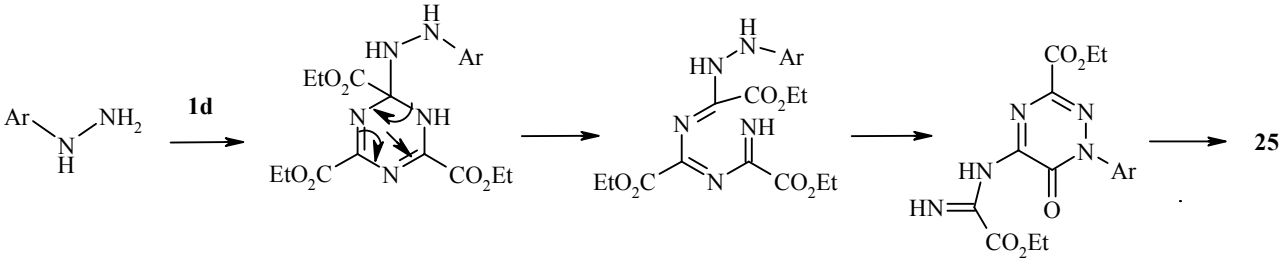


The reaction of 2,4,6-triethoxycarbonyl-1,3,5-triazine with arylhydrazines takes place differently with the participation of the ethoxycarbonyl group and leads to the formation of derivatives of 1,2,4-triazine [57]:



25

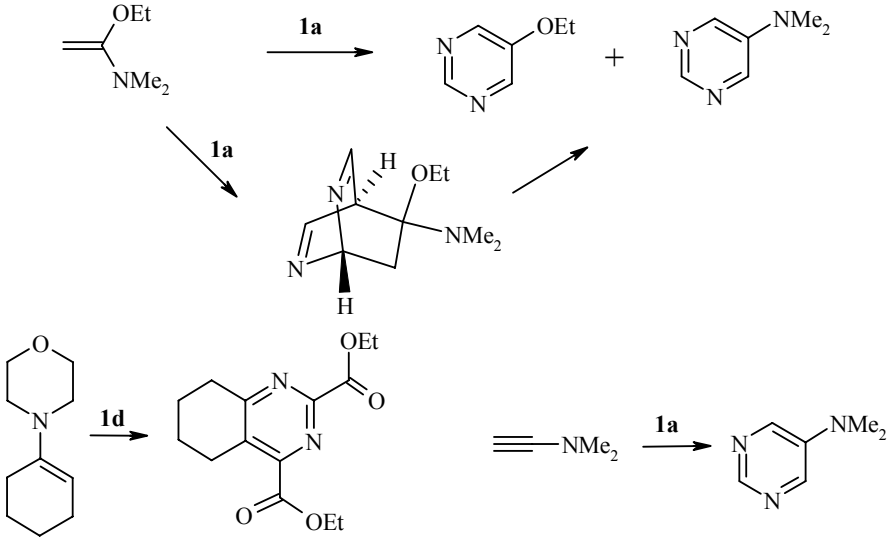
The mechanism is similar to that presented in the previous scheme, but in this case secondary attack by the nucleophile takes place at the ethoxycarbonyl group:



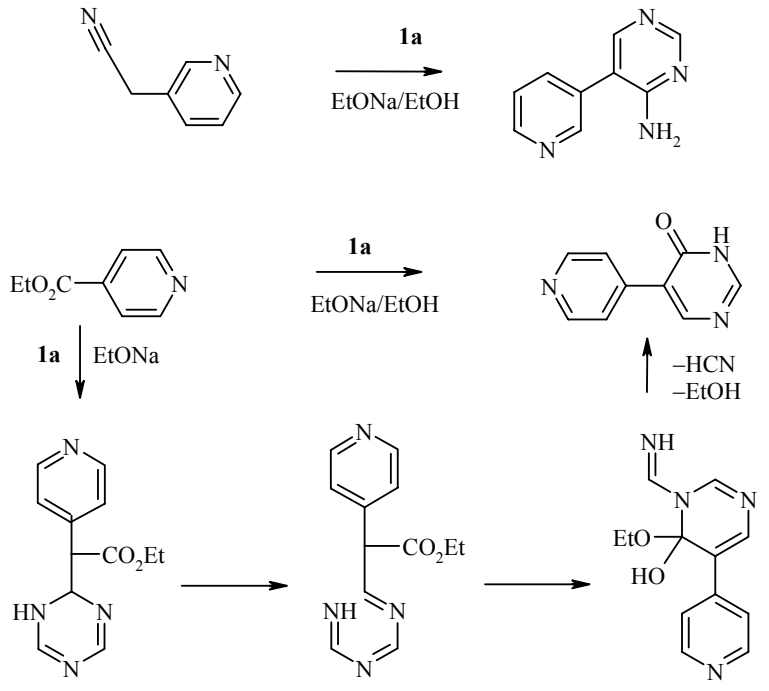
Thus, unlike the reactions with 1,4-, 1,5-, and 1,6-binucleophiles, attack in the reactions with 1,2- and 1,3-binucleophiles is realized at two different carbon atoms of the 1,3,5-triazines **1**.

4. 1,3,5-Triazines as Donors of the –CR=N–CR=N– Fragment

Such transformations are based on the ability of 1,3,5-triazines to participate in a hetero Diels–Alder reaction with the reverse electronic requirements as azadiene [58]. Various unsaturated compounds with donating substituents are used as dienophiles: Enamines [58, 59] or dialkylaminoacetylenes [60, 61]. Pyrimidines are formed in the reactions with enamines, and dialkylaminopyrimidines are formed with dialkylaminoacetylenes, for example:

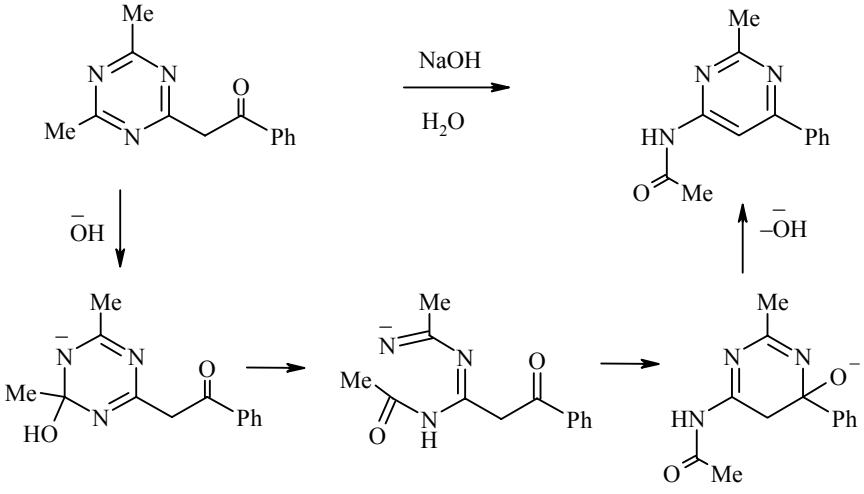


Some reactions of this type probably take place in stages. One is the formation of pyrimidines from derivatives of carboxylic acids [15, 62], for example:



Yet, in principle, these reactions can also take place by a cycloaddition mechanism.

There are a few examples of reactions in which the triazine ring is opened as a result of nucleophilic attack, and this is followed by cyclization involving a carbonyl group in the side chain [63-65], for example:



Such transformations can also be included formally among those examined in this section.

Thus, being precursors of the –CR=, –CR=N–, –CR–N=CR–, and –CR=N–CR=N– groups, 1,3,5-triazines are capable of opening as a result of reactions with various nucleophilic reagents or of cycloaddition reactions.

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