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REACTIONS OF 1,5-DIKETONES WITH AMMONIA AND ITS DERIVATIVES. (REVIEW)

V. G. Kharchenko, L. I. Markova, O. V. Fedotova, and N. V. Pchelintseva

Published data and the authors' own experimental results on the reaction of aliphatic, semicyclic, and oxosemicyclic 1,5-diketones and alkylidene- and arylidene-2,2-dicyclanones with ammonia, ammonium acetate, and XNH_2 derivatives, where X = Alk, Ar, OH, NH_2, PhNH, ArCONH, and CHO, are reviewed. The characteristics and the relationships governing the transformations into azaheterocycles in relation to the nature of the reagents and the reaction conditions are discussed.

Keywords: alkylidenedicyclanones, arylidenedicyclanones, aroylpyrroles, 3-hydroquinol-2-ones, dihydro-1,2-diazepines, N-R-dihydropyridines, dihydropyridines, tetrahydropyridines, 1,5-diketones, octahydroacridines, pentane-1,5-diones, 2-pentene-1,5-diones, pyrazolines, pyrazoles, pyridines, pyridine bases, piperidine bases, semicyclic, oxosemicyclic 1,5-diketones, pyridinium salts, tetrahydroquinolines, azaheterocyclization, indolization, pyridinization, properties, synthesis, structure.

Azaheterocycles belong to one of the most important classes of heterocyclic compounds, among which functionally useful compounds are being actively sought. Known methods for the amination of substituted 1,5-diketones and their use in the production of azaheterocycles with various degrees of saturation in the pyridine, quinoline, and acridine series include reactions with ammonia and ammonium acetate, hydroxylamine, hydrazine and its derivatives, and DMF and also catalytic hydroamination. The methods are discussed in the order indicated.

1. REACTIONS WITH AMMONIA AND AMMONIUM ACETATE

In the papers that mark the beginning of the research into the reaction of 1,5-diketones **1** with ammonia it was established that the reaction leads mainly to 1,4-dihydropyridines **2** or their possible isomers [1-6]. During study of various versions of the reaction it was found that stable products **2**, in which the heterocycle is stabilized by ester [2, 7-9], carboxyl, carbonyl [3, 10-13], or alkylthio groups [14], are only formed when the diketones **1** produced from methylene-active compounds (acetylacetone, acetoacetic ester, etc.) are used.

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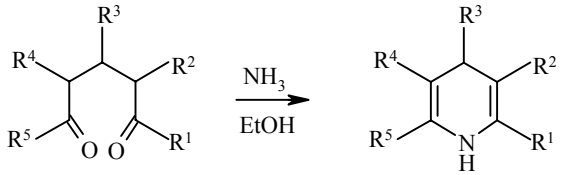
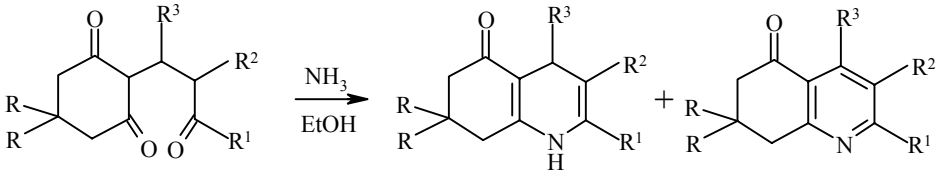


1 **2**

$R^1 = R^5 = Ph$, $R^2 = R^4 = H$, $R^3 = COOH$; $R^1 = R^5 = Me$, $R^2 = R^4 = COOEt$, $R^3 = H$; $R^1 = R^5 = Ph$, $R^2 = R^4 = COOEt$, $R^3 = Ph$; $R^1 = R^5 = Me$, $R^2 = R^4 = COMe$, $R^3 = H$; $R^1 = R^2 = R^3 = R^5 = Ph$, $R^4 = COOEt$; $R^1 = R^2 = R^3 = R^4 = R^5 = Ph$; $R^1 = R^3 = R^5 = Ph$, $R^2 = R^4 = SPh$

1,5-Diketones containing two substituents at position 3 are readily converted into 1,4-dihydropyridines [15]. From 1,5-diketones not containing electron-withdrawing groups it is not possible to obtain products of type **2** in the reaction with ammonia. In such cases under harsh conditions the pyridine bases are formed [2, 4, 15, 16]. The role of oxidant for the initially formed 1,4-dihydropyridines is played by atmospheric oxygen or by specially introduced oxidants [3, 17-19].

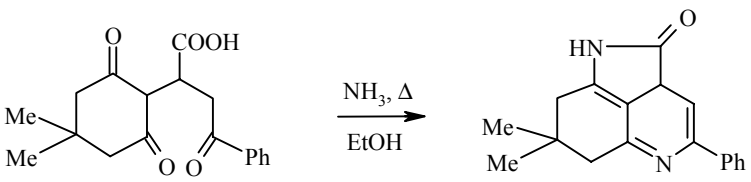
When boiled with ammonia in ethanol the semicyclic oxo-1,5-diketones (triketones) **3** and **4** form the stable 5-oxo-1,4,5,6,7,8-hexahydroquinolines **5** and **6**. This can be explained by the presence of the conjugated 6*p*π-electron fragment –CO–C=C–NH– in their molecule [20-23]. In individual cases the formation of 5-oxo-5,6,7,8-tetrahydroquinolines **7** and **8** in addition to the products **5** and **6** is possible [20-23].



3a–f, **4a–c**,**f** **5a–f**, **6a–c**,**e** **7a–f**, **8b**,**f**

3, **5**, **7** R = H; **4**, **6**, **8** R = Me; **3–8 a** $R^1 = R^3 = Ph$; **b** $R^1 = Ph$, $R^3 = p\text{-}MeOC_6H_4$; **c** $R^1 = R^3 = p\text{-}MeOC_6H_4$; **d** $R^1 = Ph$, $R^3 = p\text{-}O_2NC_6H_4$; **e** $R^1 = Ph$, $R^3 = H$; $R^1 + R^2 = (CH_2)_4$; $R^3 = H$; **3–8** $R^2 = H$

The 7,7-dimethyl-2-oxo-4-phenyl-1,2,6,7,8,8a-hexahydropyrrolo[4,3,2-*d*,*e*]quinoline **9**, related to natural alkaloids, was synthesized with a yield of 50% by heating an alcohol solution of 2-(1-carboxy-3-phenyl-3-propanon-1-yl)dimedone with ammonia in an autoclave [24].



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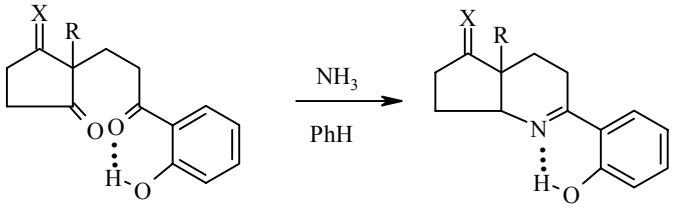
The reaction of the diketone **10a** and the triketone **10b** with ammonia in benzene resulted in the formation of the unusual products **11a**,**b** respectively [25].

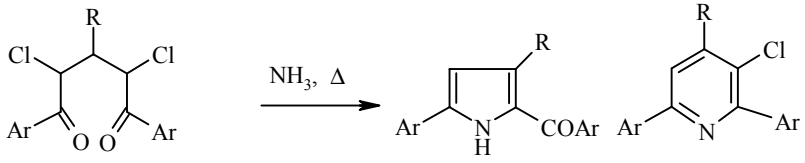


10,**b** **11**,**b**

10, **11 a** X = O, R = Me; **b** X = H_2, R = H

The stability of the latter is explained by the presence of a hydrogen bond between the nitrogen atom and the hydrogen atom of the *o*-OH group in the phenyl substituent.

Unlike their analogs **1** (R^2 = R^4 = H), the 2,4-dichloro-substituted 1,5-diketones **12a-f** react with ammonia in dioxane at 60°C (and the ketone **12b** also in a mixture of alcohol and benzene) with the formation of the aroylpyrroles **13a-f** (yields 47-80%); in the case of the diketones **12d-f** small amounts of the 3-chloropyridines **14d** (16%) and **14f** (9%) are also obtained [26-28].

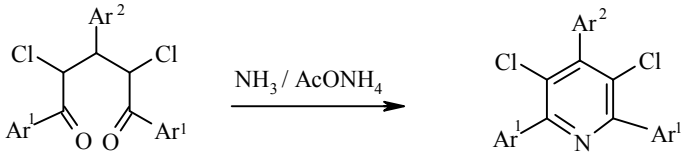


12a–f **13a–f** **14d**,**f**

12, **13 a** Ar = Ph, R = H; **b** Ar = *p*-$MeOC_6H_4$, R = H; **c** Ar = *p*-ClC_6H_4, R = H; **e** Ar = R = Ph;
12–14 d Ar = Ph, R = Me; **f** Ar = Ph, R = *p*-ClC_6H_4

On the other hand, with ammonia or ammonium acetate in acetic acid at 60-80°C the dichloro diketones **12a**,**c-e** form mostly the monochloropyridines **14a**,**c-e** (yields 79-92%), and only from the diketone **12c** was the aroylpyrrole **13c** obtained with a yield of ~9%. The reaction of the dichloro diketones **12a**,**d**,**e** with ammonium acetate in dioxane (60°C) gives mixtures in which the contents of the chloropyridines **14a**,**d**,**e** amount to 58, 68, and 67% and the contents of the pyrroles **13a**,**d**,**e** amount to 34, 37, and 21% respectively [26-28].

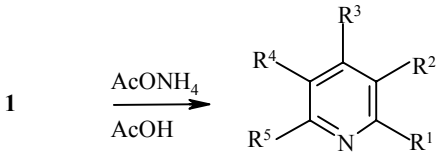
In reaction with ammonia in dioxane at 60°C or with ammonium acetate in acetic acid at 80°C the unsaturated 1,3,5-triaryl-2,4-dichloro-1,5-diketones **15a-d** are converted into 2,4,6-triaryl-3,5-dichloropyridines **16a-d** [28-30].



15a–d **16a–d**

15, **16 a** Ar^1 = Ar^2 = Ph; **b** Ar^1 = *p*-ClC_6H_4, Ar^2 = Ph; **c** Ar^1 = Ph, Ar^2 = *p*-ClC_6H_4;
d Ar^1 = Ph, Ar^2 = *p*-$MeOC_6H_4$

Numerous investigations have been devoted to the reactions of the diketones **1** with ammonium acetate in acetic acid (the improved Chichibabin synthesis). This is explained by the effectiveness of this method for the production of pyridine bases of type **17** and in a number of cases piperidine or tetrahydropyridine bases [7, 16, 31-43].



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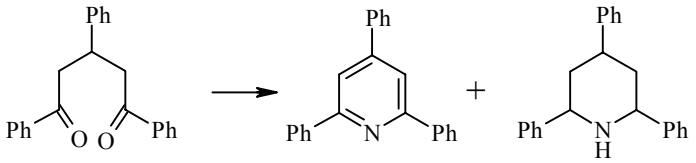
$R^1 = R^3 = R^5 = Ph$; $R^1 = R^5 = Ph$, $R^3 = p$-$MeOC_6H_4$; $R^1 = R^5 = Ph$, $R^3 = m,p$-$(OCH_2O)C_6H_3$;
$R^1 = R^5 = Ph$, $R^3 = p$-$Me_2NC_6H_4$; $R^1 = R^5 = Ph$, $R^3 = o$-$MeOC_6H_4$; $R^1 = R^5 = \beta$-$C_{10}H_7$, $R^2 = Ph$;
$R^1 = R^5 = \beta$-$C_{10}H_7$, $R^3 = \alpha$-furyl; $R^1 = R^2 = R^3 = R^4 = R^5 = Ph$; $R^3 = Ph$,
$R^4 + R^5 = o$-$(CH_2)_2C_6H_4 = A$; $R^1 + R^2 = (CH_2)_3$, $R^3 = Ph$, $R^4 + R^5 = A$; $R^1 + R^2 = (CH_2)_4 = B$,
$R^3 = Ph$, $R^4 + R^5 = A$; $R^1 + R^2 = B$, $R^4 + R^5 = A$; $R^4 + R^5 = B$; not indicated R = H

The formation of the piperidines or tetrahydropyridines, together with the pyridines, is explained by the ability of the unstable 1,4-dihydropyridines that form to undergo disproportionation [21, 25, 32, 34]:



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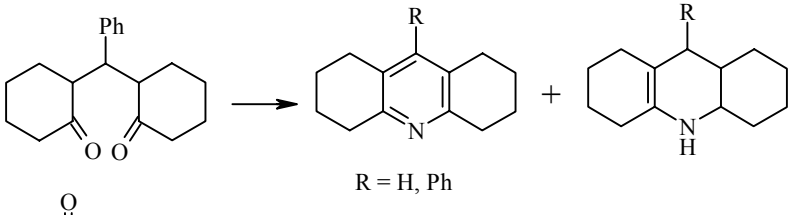
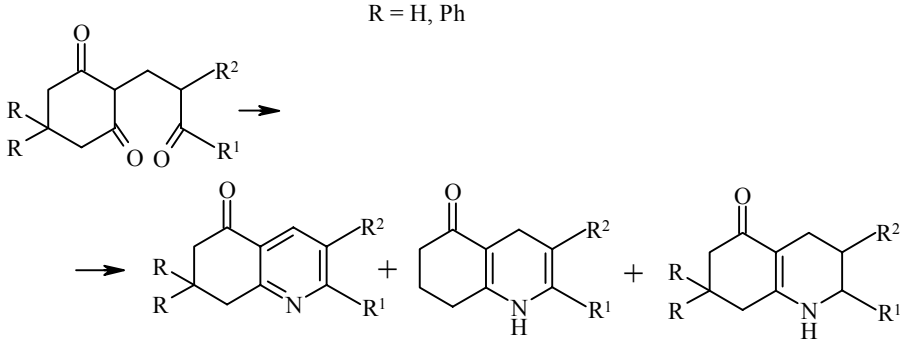


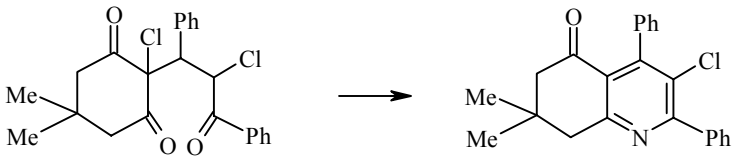
R = H, Ph



R = H, Me; R^1 = Ph, R^2 = H; $R^1 + R^2 = (CH_2)_4$

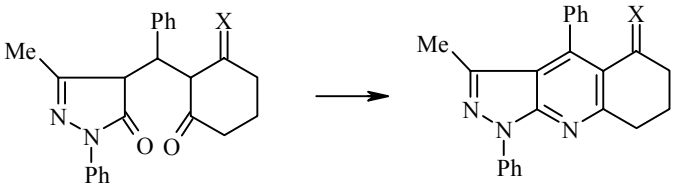
The above-mentioned semicyclic oxo 1,5-diketones **3a-c** and **4a-c** and also the triketones **3g** and **4g** (R^1 = Ph, $R^3 = p$-$O_2NC_6H_4$) under the influence of ammonium acetate in acetic acid form the corresponding pyridinization products – 5-oxotetrahydroquinolines **7a-e**,**g** and **8a-c**,**g**, in contrast to the triketone **3d**, which is transformed into 5-oxo-1,4,5,6,7,8-hexahydroquinoline **5d**. The stability of the latter can be explained by the presence of the electron-withdrawing substituent (the p-$O_2NC_6H_4$ group) at position 4 of the dihydropyridine ring [44-46].

The monochlorine-substituted oxotetrahydroquinoline **20** is produced with a yield of 68% from the dichlorine-substituted oxo 1,5-diketone **19** and ammonium acetate in glacial acetic acid at 105°C [44].



19 **20**

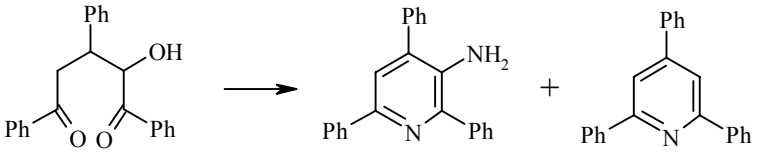
When heated with ammonium acetate in acetic acid the 1,5- and oxo 1,5-diketones **21**, containing a pyrazolone ring, form the pyrazolo[4,5-*b*]-5,6,7,8-tetrahydroquinolines **22** [47].



21 **22**

X = H_2, O

Under analogous conditions the triphenyl-substituted 2-hydroxypentane-1,5-dione **23** undergoes unusual transformations to 3-aminotriphenylpyridine and triphenylpyridine [48].



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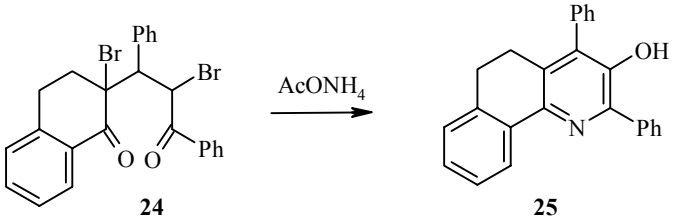
During the action of ammonium acetate on the dibromo diketone **24** the initially formed product not only undergoes pyridinization, but one bromine atom is replaced by a hydroxyl group with the formation of the substituted dihydrobenzoquinone **25** [49].



24 **25**

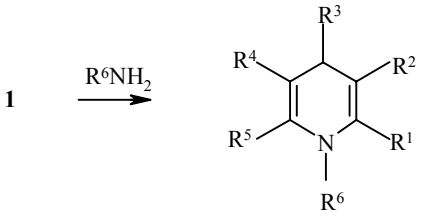
The presented examples of the reaction of 1,5-diketones with ammonia and ammonium acetate demonstrate the considerable possibilities of a directed synthesis of various azaheterocycles: 1,4-dihydropyridines, aroylpyrroles, pyridines.

2. REACTIONS OF 1,5-DIKETONES WITH PRIMARY AMINES

A detailed investigation of the reaction of various 1,5-diketones with primary alkyl- and arylamines [50] showed that the ease of the reaction depends on the nature of the initial reagents. It was established that the ease of the reaction decreases in the following order: alicyclic dioxo compounds, methylenebiscyclohexanones and their analogs > semicyclic 1,5-diketones > aliphatic-aromatic 1,5-diketones. The reactions of the latter with primary amines were studied earlier [5], but the structure of the obtained products was not adequately proved. Substitution of the six-membered alicycle by a five-membered ring leads to a significant decrease in the activity of the bicyclic 1,5-diketones. Primary aliphatic amines are more reactive than aromatic amines, and among the latter compounds with electron-donating substituents in the benzene ring are more active than those with electron-withdrawing substituents.

The nature of the products is determined by the specific group of compounds to which the initial diketones (aromatic-aliphatic, semicyclic, alkylidene- and arylidenedicyclanones, etc.) and also the amines (aliphatic, aromatic, etc.) belong.

With primary amines, as also with ammonia, the 1,5-diketones **1** produced from methylene-active compounds form N-substituted 1,4-dihydropyridines **26**, containing electron-withdrawing groups at positions 3 and 5 [51-55].



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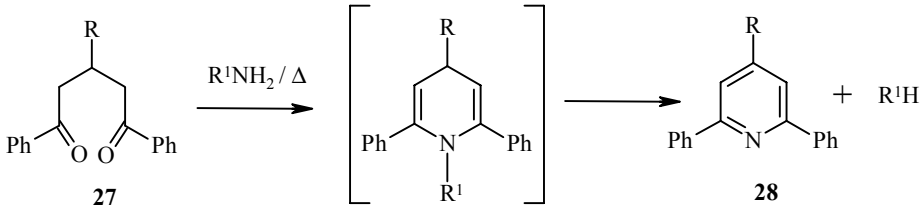
1, **26** $R^1 + R^2 = R^4 + R^5 = CH_2–CMe_2–S–CH_2$, $R^3 = H$, $R^6 = PhCH_2$;
$R^3 = Me$, $R^6 = PhCH_2$, $R^3 = Ph$, $R^6 = PhCH_2$, $R^3 = Ph$, $R^6 = cyclo\text{-}C_6H_{11}$, $R^3 = 4\text{-}MeOC_6H_4$,
$R^6 = PhCH_2$, $R^3 = Ph$, $R^6 = PhCH_2$, $R^1 = \alpha$-thienyl, $R^2 = R^5 = (CH_2)_4$, $R^6 = PhCH_2$

1,4-Dihydropyridines not containing electron-withdrawing substituents are unstable [56, 57].

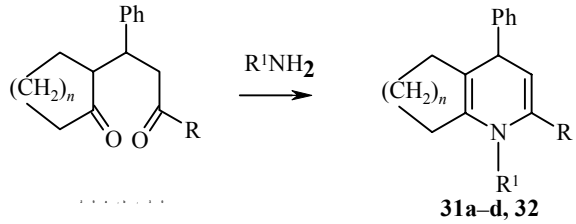
In the case of aromatic-aliphatic 1,5-diketones **27** the initially formed 1,4-dihydropyridines are often pyridinized, resulting in the production of the pyridines **28** [5, 50].



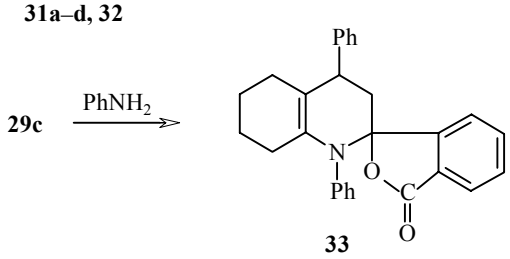
27 **28**

R = H, Ph; R^1 = Ph, Et

The respective N-substituted 5,6-tetra(penta)methylenedihydropyridines **31a-d** and **32** were obtained from the semicyclic 1,5-diketones **29a**,**b** and **30** and primary aromatic amines [50, 58-60]. The spiro compound **33** is formed from the diketone **29c** and aniline [50]:



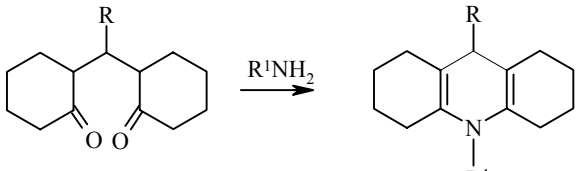
31a–d, 32



33

29a-c n = 2; **a** R = Ph; **b** R = α-thienyl; **c** R = *o*-$HOOCC_6H_4$; **30** n = 3; R = Ph; **31a-d** n = 2, **a** R = α-thienyl, R^1 = Ph; **b** R^1 = α-naphthyl, **c** R^1 = *p*-$MeOOC_6H_4$, **d** R^1 = $PhCH_2$; **32** n = 3, R = R^1 = Ph

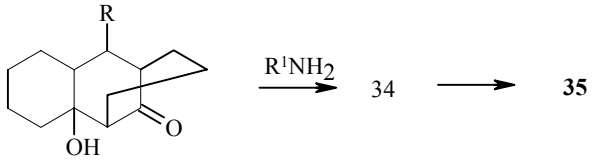
A distinguishing feature of the 1,5-diketones containing a methyl or methylene group at the α-position is the ability to undergo intramolecular cyclization of the aldol condensation type, which takes place readily in the series of α-R-methylenedicyclohexanones [33]. Till now the latter have been difficult to obtain, since even traces of alkali lead to their aldolization. The β-cycloketols that are formed readily undergo retroaldol dissociation on heating in the presence of bases, and this makes them analogs of 1,5-diketones in various reactions, including amination. The most active in the reactions are alkylidenedicyclohexanones. Thus, methylene- and ethylidenedicyclohexanones **34** react with primary aromatic amines without heat in a water–alcohol solution, forming mainly 2,3,5,6-bis(tetramethylene)-1,4-dihydropyridine systems **35** (R = H, Me) [50, 61]. Similar products (R = Ar) were also obtained from arylidenecyclohexanones by boiling in benzene or xylene [50].



34 **35**

34 R = H, Me, Ph, *p*-$MeOC_6H_4$, *p*-$Et_2NC_6H_4$; **35** R = H, Me, R^1 = Ph, *p*-$Et_2NC_6H_4$, *p*-HOC_6H_4, *m*-BrC_6H_4, *p*- $O_2NC_6H_4$, *p*-$MeOOCC_6H_4$, β-hydroxy-α-naphthyl; R = *p*-$MeOC_6H_4$, R^1 = Ph, *p*-$Et_2NC_6H_4$, R = *p*-$Me_2NC_6H_4$, R^1 = Ph

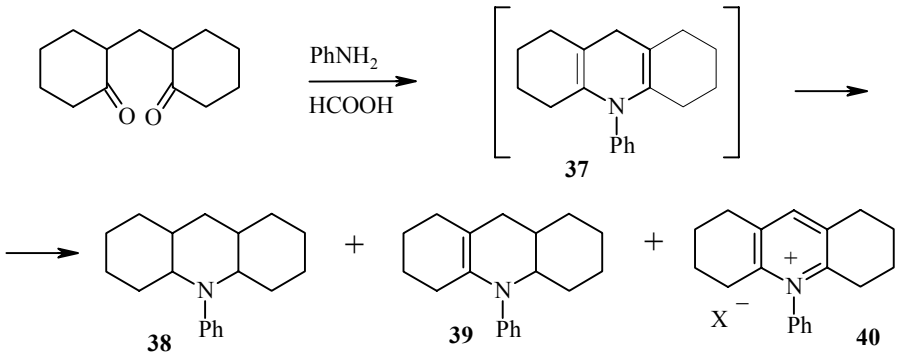
Arylidenecyclohexanones **34** are difficult to obtain. They are formed during the decyclization of the respective β-cycloketols **36**, which react with primary amines in the presence of a catalyst (TsOH) as 1,5-diketones [50, 62].



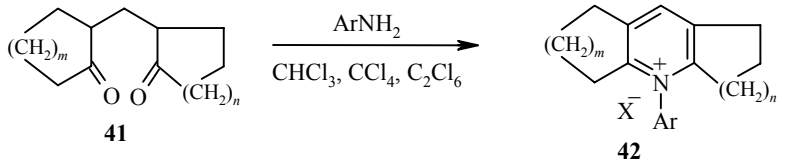
36

R = Ph, R^1 = $PhCH_2$, C_6H_{11}; R = *p*-$MeOC_6H_4$, R^1 = $PhCH_2$

When heated with aliphatic amines in acetic acid the diketones **34** (R = H, Ph) often form N-R^1-*sym*-octahydroacridines of type **35** (R^1 = Me, $HOCH_2CH_2$, $EtOOCCH_2$) or mixtures of the latter with the respective decahydroacridines [50, 61-63]. In the case of aromatic amines in acetic acid the initially formed N-R^1-*sym*-octahydroacridines disproportionate to the corresponding N-R^1-dodecahydroacridines and N-R^1-octahydroacridinium salts [61]. Under the influence of aniline in formaldehyde methylenebiscyclohexanone is transformed through N-Ph-octahydroacridine **37** into N-Ph-substituted perhydroacridine **38**, dodecahydroacridine **39**, and the *sym*-octahydroacridinium salt **40**, which was isolated in the form of the perchlorate [64-66]

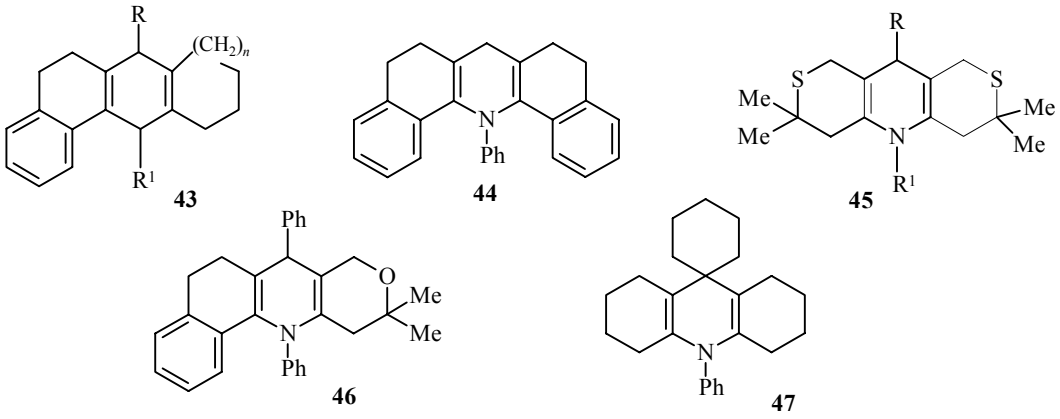


The reaction of aromatic amines with the diketones **41** in the presence of chloroform, tetrachloromethane, or hexachloroethane leads to the arylpyridinium salts **42**, which are isolated in the form of chlorides or perchlorates [50, 54-64, 67, 68].



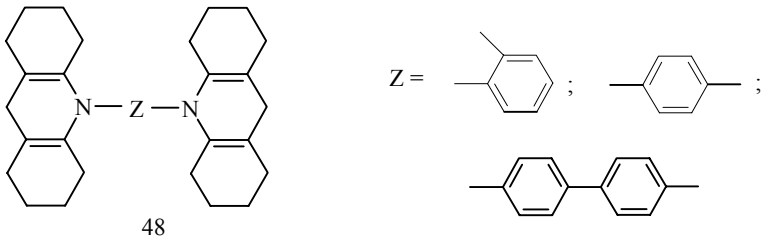
n = 1, 2; *m* = 2, 3; X^- = Cl, ClO_4, Ar = Ph, *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$, *p*-$HOOCC_6H_4$, $PhCH_2$, α-$C_{10}H_7$, β-$C_{10}H_7$

A series of polycondensed systems **43**-**47** were also constructed on the basis of various 1,5-diketones [50].



43 *n* = 1, R = H, R^1 = Ph, α-naphthyl, *p*-$MeOOCC_6H_4$; *n* = 2; R = H, R^1 = naphthyl, *p*-$HOOCC_6H_4$; R = R^1= Ph; R = Ph, R^1 = *p*-$MeOOC_6H_4$; R = Ph, *p*-$MeOC_6H_4$, *p*-$MeOOCC_6H_4$; **45** R = H, Me, R^1 = *p*-$MeOOCC_6H_4$

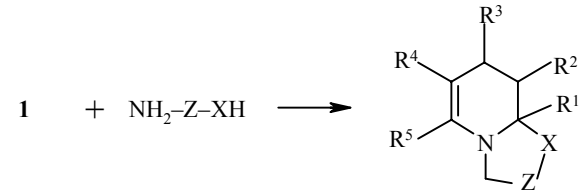
Arylidenedidecahydroacridines **48** were synthesized from methylene-2,2'-dicyclohexanone and diamines, such as *o*- and *p*-phenylenediamine and benzidine [58].



48

In the reaction of 1,5-diketones with amines containing an additional nucleophilic center the latter can also participate in the reaction, leading to more complex products.

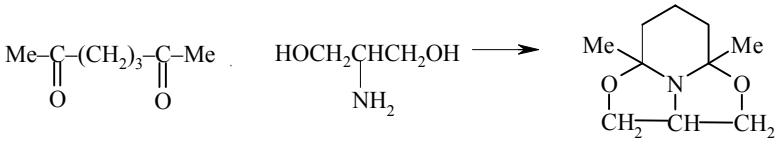
The so-called "double cyclization," shown in the general scheme below, was developed on a large number of examples [50, 69-79] of the reaction of aromatic-aliphatic semi- and polycyclic 1,5-diketones with bifunctional amines of the aliphatic and aromatic series containing hydroxyl, carboxyl, or a second amino group.



$R^1 = R^5 = Ph$, $R^2 = R^3 = R^4 = H$, X = NH, O, Z = *o*-phenylene; $R^1 + R^2 = (CH_2)_4$, $R^3 = H$, Ph,
$R^4 = H$, $R^5 = Ph$, X = O, Z = $(CH_2)_2$, X = COO, Z = *o*-phenylene; $R^1 + R^2 = (CH_2)_4$, $R^3 = H$, Ph,
$R^4 + R^5 = o\text{-}(CH_2)_2C_6H_4$, X = O, COO, Z = *o*-phenylene, α,β-naphthylene;
$R^1 + R^2 = R^4 + R^5 = (CH_2)_4$, X = O, Z = $(CH_2)_3$

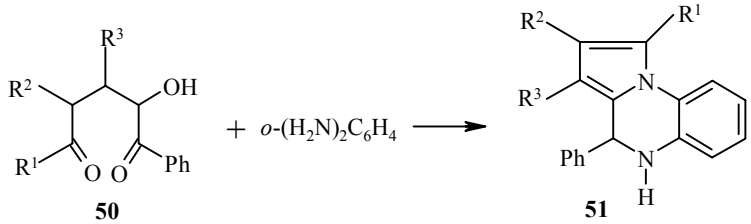
In view of the fact that the double cyclization reactions are of the same type and in view of the large number of compounds obtained, the values of R, X, and Z given below the scheme only illustrate the individually known cases where products containing a nitrogen-containing heterocycle are formed.

The reaction of heptane-2,6-dione and 2-aminopropane-1,3-dione containing three functional groups resulted in the formation of the tricyclic compound **49** [80].



49

The participation of the three functional groups of 2-hydroxy 1,5-diketones **50** and the two NH_2 groups of *o*-phenylenediamine in the reaction led to 4,5-dihydropyrrolo[1,2-*a*]quinoxalines **51** [50].

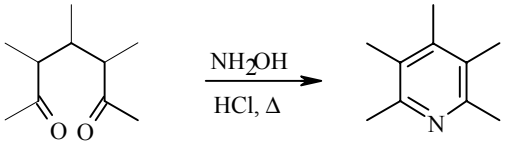


50 **51**

$R^1 = R^3 = Ph$, $R^2 = H$; $R^1 = Ph$, $R^2 = H$, $R^3 = Me$; $R^1 = Ph$, $R^2 = R^3 = H$;
$R^1 = R^2 = (CH_2)_4$, $R^3 = Ph$

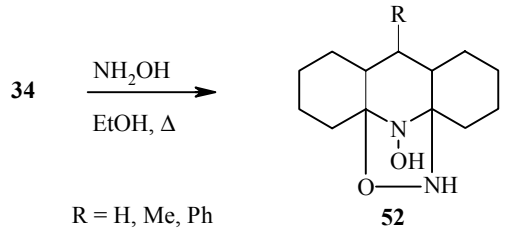
3. REACTIONS OF 1,5-DIKETONES WITH HYDROXYLAMINE

Knoevenagel first established that when 1,5-diketones were heated with hydroxylamine hydrochloride the corresponding pyridines were formed (Knoevenagel–Stobbe pyridinization) [2, 7, 81]. This method can be applied to aliphatic [81-83], bicyclic [31, 84-86], semicyclic [87-90], and aromatic-aliphatic [2, 91, 92] 1,5-diketones and oxo 1,5-diketones of the semicyclic series [93-95].

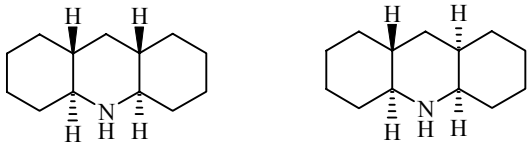


In the presence of bases from 1,5-diketones and hydroxylamine monoximes [88], dioximes [83, 91, 96, 97], or (in the case of semicyclic oxo-1,5-diketones) trioximes [44], which also undergo pyridinization under the influence of hydrochloric acid or hydrogen chloride, are formed. Tetrahydroquinoline oximes are formed from the trioximes.

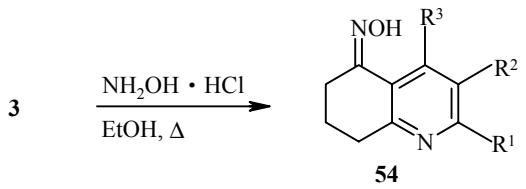
The exception is the above-mentioned 2,2'-alkylidene(arylidene)dicyclohexanones [75]. Their reaction with two equivalents of hydroxylamine in the presence of bases at normal temperature leads not to dioximes, as supposed earlier [98, 99], but to the tetracyclic compounds **52** [100], the structure of which was confirmed by chemical transformations [96].



Thus, the α- and β-stereoisomers of the product **52** (R = H), corresponding to the *meso* and racemic forms of the initial diketone, were obtained from methylene-2,2'-dicyclohexanone [57]. During reduction with sodium in butanol the *trans-syn-trans* isomer was obtained from the α-isomer **52**, while the *trans-anti-cis* isomer of perhydroacridine **53a** and **53b** respectively was obtained from the β-isomer of **52**.



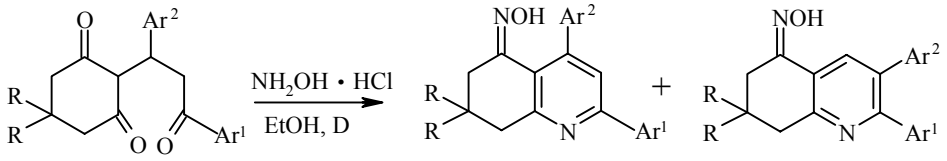
The nature of the reaction of the oxo-1,5-diketones (triketones) with hydroxylamine hydrochloride in alcohol (boiling) is determined by the position and the nature of the substituents in the propanonyl fragment. If R^3 = H or R^3 = *p*-$O_2NC_6H_4$ pyridinization occurs, and the corresponding 5,6,7,8-tetrahydroquinoline oximes **54** are formed [93-95, 101, 102].



54

R^1 = Ph, R^2 = R^3 = H; R^1 = Ph, R^2 = Me, R^3 = H; $R^1 + R^2 = (CH_2)_4$, R^3 = H;
R^1 = Ph, R^2 = H, R^3 = *p*-$O_2NC_6H_4$

Under similar conditions with a threefold excess of hydroxylamine hydrochloride diaryl-substituted triketones of types **3** and **4** undergo pyridinization accompanied by anionotropic rearrangement. As a result the expected 1,3-diaryl-5-oxo-5,6,7,8-tetrahydroquinoline oximes **55** and **56** and their isomeric 2,3-diaryl-5-oxo-5,6,7,8-tetrahydroquinoline oximes **57** and **58** are formed [93-95].



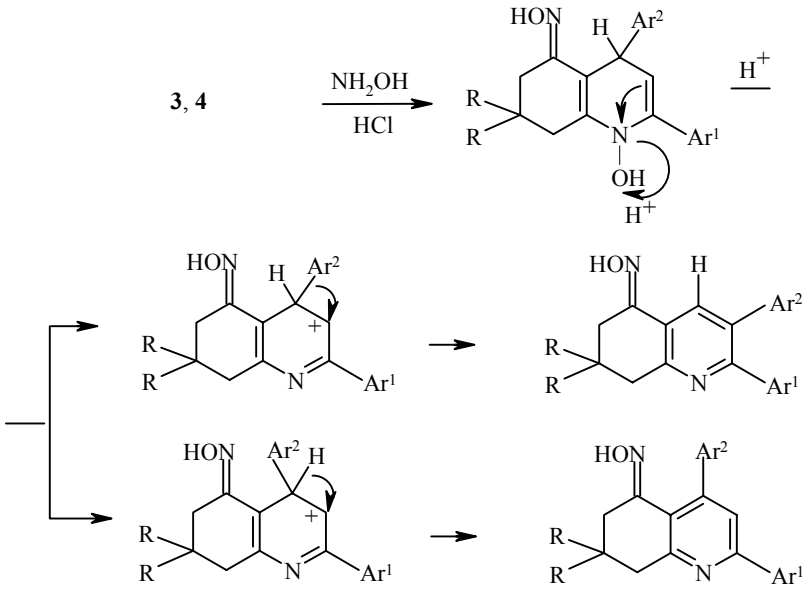
3a–d, **4a–c** **55a–d**, **56a–c** **57a–d**, **58a–c**

3, **55**, **57** R = H, **4**, **56**, **58** R = Me; **3**, **4**, **55–58 a** Ar^1 = Ar^2 = Ph; **b** Ar^1 = *p*-$MeOC_6H_4$, Ar^2 = Ph; **c** Ar^1 = Ar^2 = *p*-$MeOC_6H_4$; **3, 55, 57 d** Ar^1 = *p*-$MeOC_6H_4$, Ar^2 = Ph

The presence of the electron-donating methoxy group in Ar^1 and Ar^2 promotes the rearrangement and leads to a twofold increase in the yield of the isomers **57** and **58** [95]. In the case of an electron-withdrawing NO_2 group in Ar^1 or Ar^2 the rearrangement does not occur [95].

It was shown that the yield of the isomeric oxime **58c** is affected by the solvent: In acetic acid the ratio of the oximes is 1:3, while in ethanol it is 1:2. Consequently, the acetic acid promotes the formation of the rearrangement product **58c**, which is evidently due to the increased acidity of the medium.

The following scheme was proposed for the rearrangement [94]:

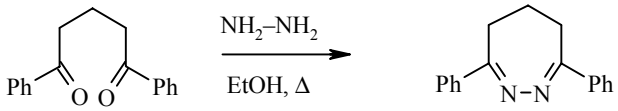


The structure of the oxime was confirmed by the data from X-ray crystallographic analysis and spectral and chemical methods [94].

4. REACTIONS OF 1,5-DIKETONES WITH HYDRAZINE AND PHENYLHYDRAZINE

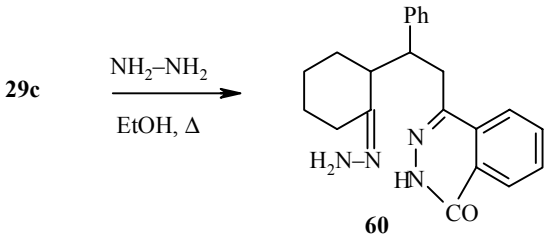
Hydrazine is of particular interest as a reagent in reactions with 1,5-diketones, since it makes it possible to realize the synthesis of five-, six-, and seven-membered heterocycles containing one or two nitrogen atoms. The literature contains data on the nature of the reaction of aliphatic-aromatic semicyclic and bicyclic 1,5-diketones and oxo-1,5-diketones with hydrazine hydrochloride, hydrazine hydrate, and phenylhydrazine under various conditions.

It was established that the direction of the process is determined by the structure of the employed reagents and by the reaction conditions (the nature of the solvent, the temperature). Thus, with hydrazine hydrate boiled in ethanol 1,5-diphenylpentane-1,5-dione forms dihydro-1,2-diazepine **59** [103, 104]:



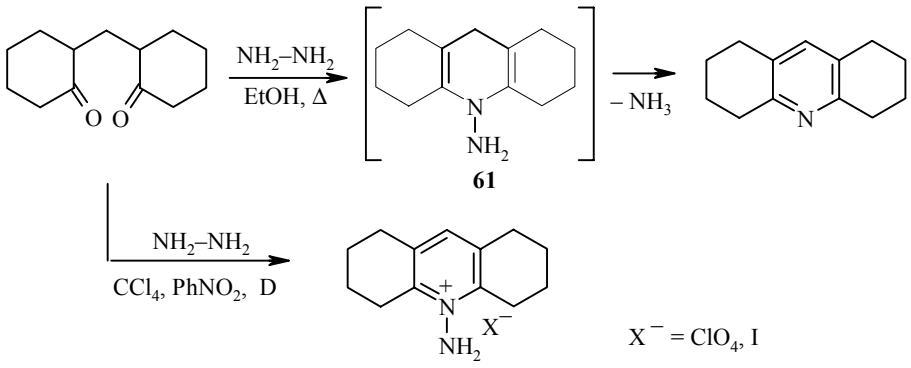
59

In the case of the semicyclic 1,5-diketone **31c** the hydrazonophthalazone **60** was obtained with any ratio of the reagents [105].



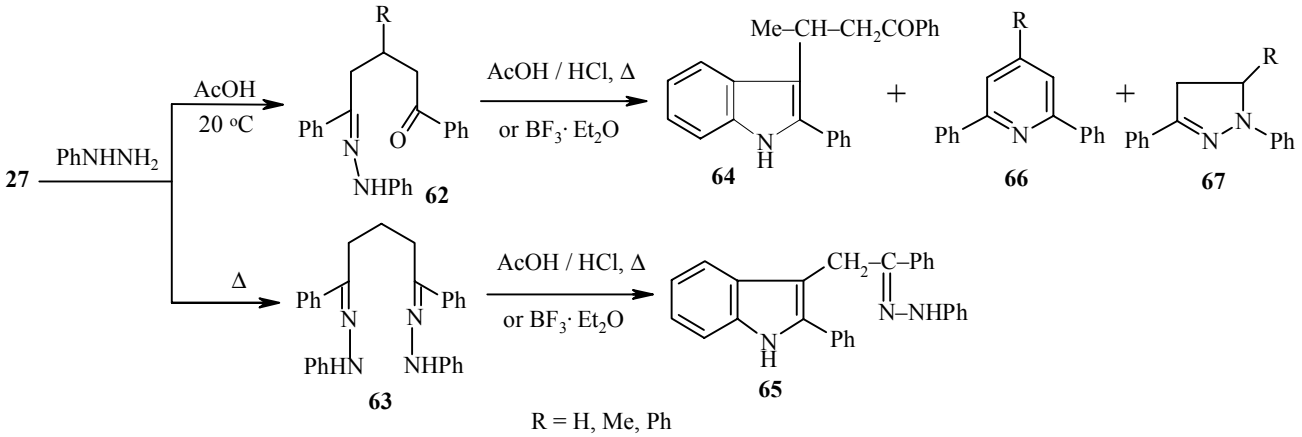
60

The reaction of methylenedicyclohexanone with hydrazine hydrate under very mild conditions leads to *sym*-octahydroacridine, which is probably formed as a result of the elimination of ammonia from the initially formed N-aminodecahydroacridine (**61**) and pyridinization of the heterocycle, while in the presence of hydride ion acceptors the process results in the formation of a 10-amino-*sym*-octahydroacridinium salt [106].



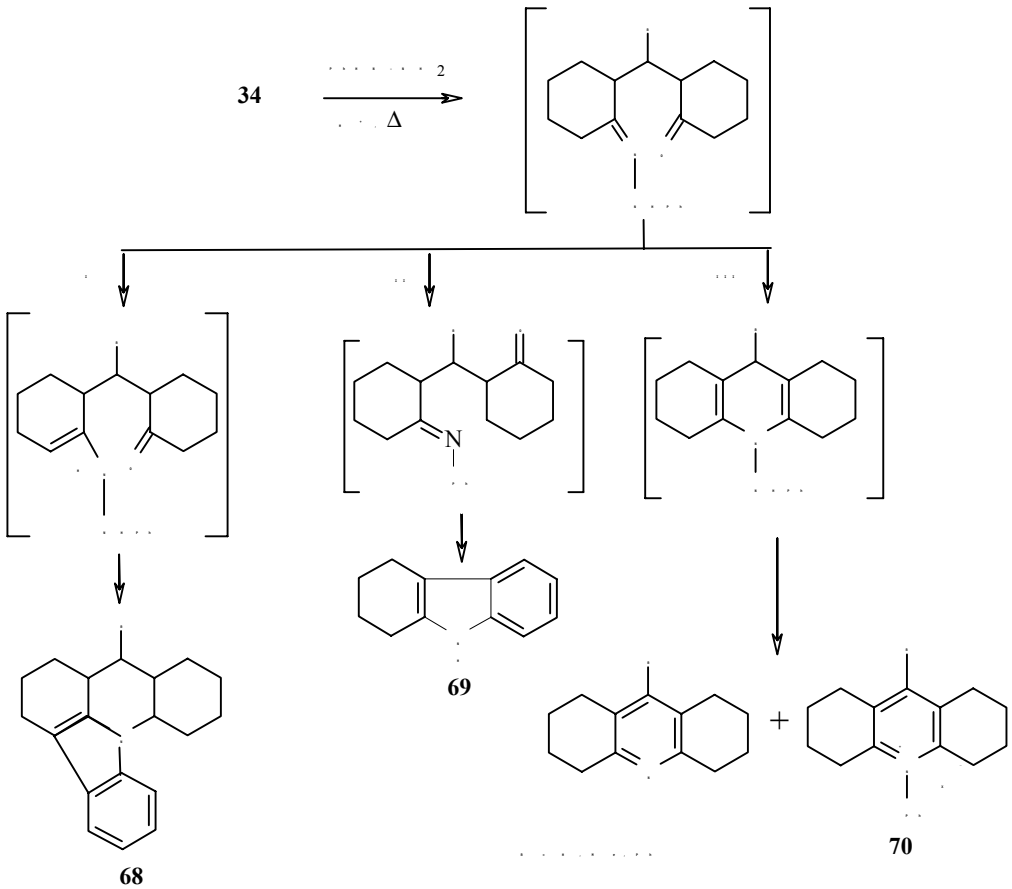
61

Aromatic-aliphatic 1,5-diketones of type **27** with phenylhydrazine at room temperature in acetic acid form monophenylhydrazones **62**. Bisphenylhydrazine **63** could only be obtained by heating 1,5-diphenylpentane-1,5-dione with an excess of phenylhydrazine in acetic acid [107]:



When compounds **62** and **63** are heated in acetic acid, treated with acetic acid saturated with hydrogen chloride, or subjected to the action of boron trifluoride etherate, their transformations take place in different ways. Indolization products **64** and **65** are only obtained from the monophenylhydrazone **62** (R = Me) and

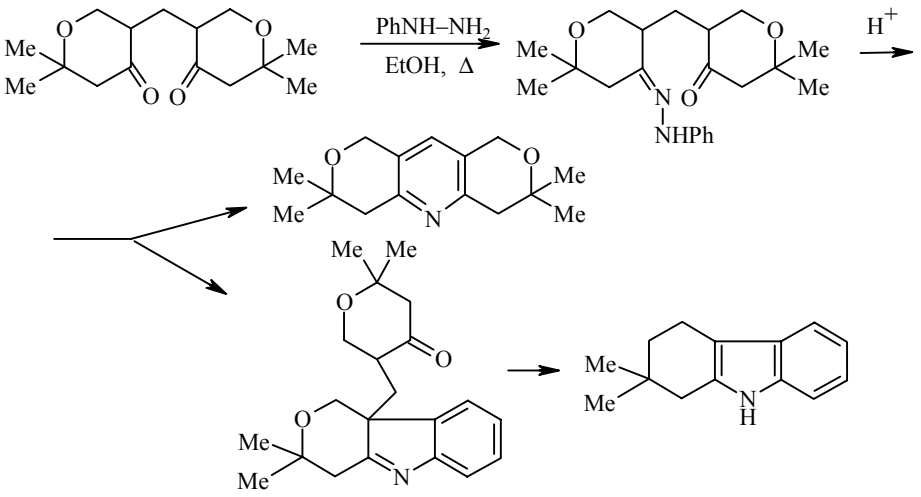
Scheme 1



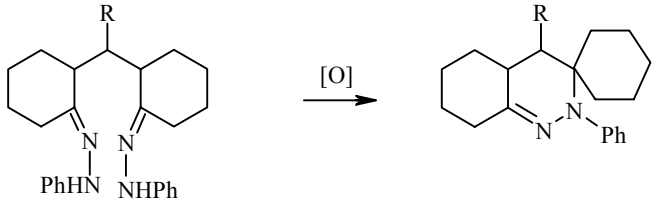
diphenylhydrazone **63** respectively. In the case of the phenylhydrazones **62** pyridinization to the respective pyridines **66** occurs, and the pyrazolines **67** (with R = Me, Ph) are formed. This results from a retro-Michael dissociation of the hydrazones **62** (or the initial diketones) followed by reaction with phenylhydrazine [107].

During the action of phenylhydrazine in an acidic medium bicyclic 1,5-diketones of type **34** undergo complex transformations; as well as indolization and the formation of condensed indoles **68** and **69** (paths I and II) there is also a transformation to *sym*-octahydroacridines and the corresponding salts **70** (path III) [108] (Scheme 1).

Methylene-3,3'-bis(5,5-dimethyl-4-oxotetrahydropyranyl) reacts with phenylhydrazine like the previously discussed diketones **34** [108]:

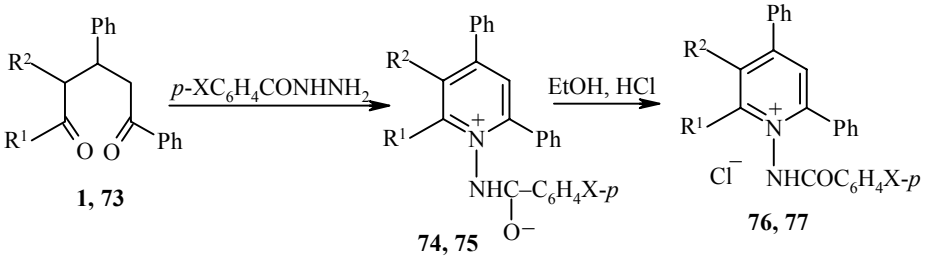


The bisphenylhydrazones **71**, obtained from the diketones **34** in an alkaline medium, undergo cyclization during the action of oxidants (oxygen or ferric chloride) to the substituted $\Delta^{1(9)}$-octahydrocinnoline-3-spirocyclohexanes **72** [109].



71 R = H, Me, Ph **72**

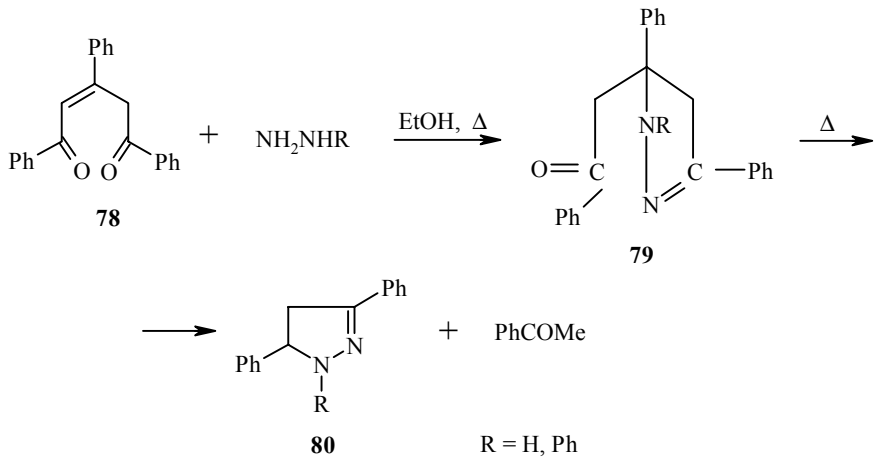
The reaction of the aromatic-aliphatic diketone **1** or the semicyclic diketone **73** with aroylhydrazines leads to the corresponding betaines **74** and **75**, which are transformed into the salts **76** and **77** when treated with alcohol saturated with hydrogen chloride [110].



1, 73 **74, 75** **76, 77**

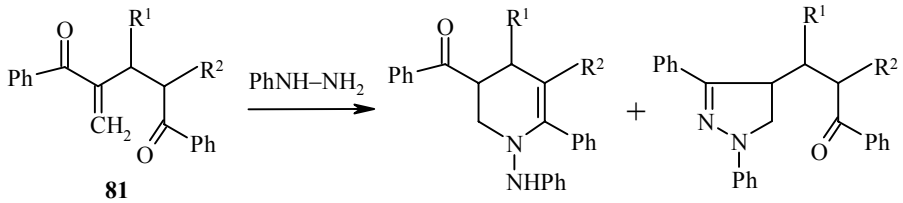
1, **74**, **76** R^1 = Ph, R^2 = H; **73**, **75**, **77** $R^1 + R^2 = CH_2CMe_2OCH_2$; **74**–**77** X = H, Cl, NO_2

Unsaturated 1,5-diketones form unusual products with hydrazine and phenylhydrazine. Thus, in the case of the substituted pentenedione **78** the pyrazolines **79** are obtained. When heated above the melting point or recrystallized from acetic acid the latter dissociate into the substituted pyrazole **80** and acetophenone [111-113].



78 **79** **80** R = H, Ph

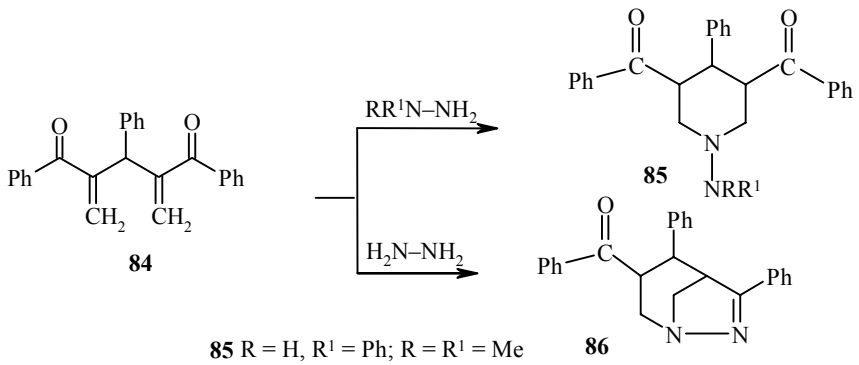
2-Methylenepentane-1,5-diones **81** react with phenylhydrazine at two groups (methylene and 5-carbonyl) with the formation of products whose dehydration leads to N-aminophenyl-5-phenacyltetrahydropyridines **82**. In the case of diketones (R^1 = R^2 = H, R^1 = Ph, R^2 = H) 4-(3-phenyl-3-oxopropyl)-1,3-diphenylpyrazolines **83** were also isolated [114].



81 **82** **83**

81, **82** R^1 = H, Ph; R^2 = H, CH_2NMe_2, CH_2N O ; **83** R^1 = R^2 = H; R^1 = Ph, R^2 = H

The reaction of 2,4-dimethyl-1,3,5-triphenylpentane-1,5-dione **84** with phenylhydrazine or N,N-dimethylhydrazine leads to the formation of stereoisomeric N-substituted 3,5-dibenzoyl-4-phenylpiperidines **85** [114]:



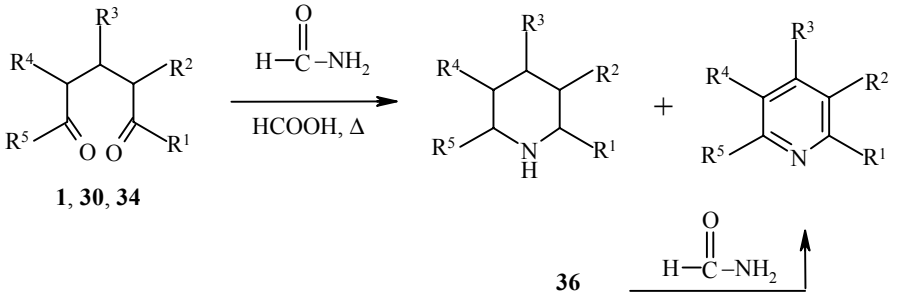
84 **85** **86**

85 R = H, R^1 = Ph; R = R^1 = Me

The reaction of the diketone **84** with hydrazine resulted in the production of a bicyclic product with a bridgehead nitrogen atom **86** [114].

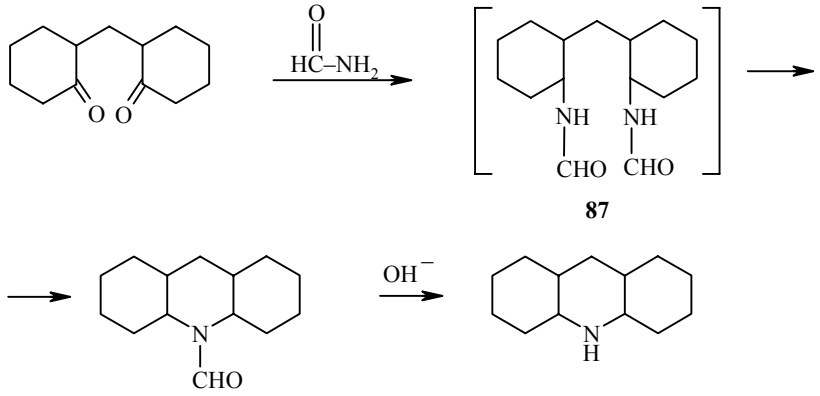
5. 1,5-DIKETONES IN THE LEUCKART REACTION

The Leuckart reaction, which involves reaction (130-170°C) of a solution of the 1,5-diketone or its cycloketolization product **36** with formamide [115, 116] or with an excess of a mixture of ammonium formate and formamide [34], in all cases leads predominantly to piperidine derivatives [16, 31, 115, 116]. It is assumed that the corresponding 1,4-dihydropyridine is formed initially and disproportionates to a mixture of piperidine and pyridine bases [31, 34, 117, 118]. Thus, from diketones of types **1**, **30**, and **34** certain amounts of pyridine derivatives were obtained in addition to the piperidine derivatives [16, 31, 34, 119].



1 $R^1 = R^5 = Ph$; $R^1 = R^3 = R^5 = Ph$; $R^1 = R^5 = p\text{-}MeOC_6H_4$, $R^3 = o,p,o\text{-}(MeO)_3C_6H_2$;
30 $R^1 = R^3 = Ph$, $R^4 + R^5 = (CH_2)_4$; **34** $R^1 + R^2 = R^4 + R^5 = (CH_2)_4$; **36** R = Me, Ph, α-furyl; not indicated R = H

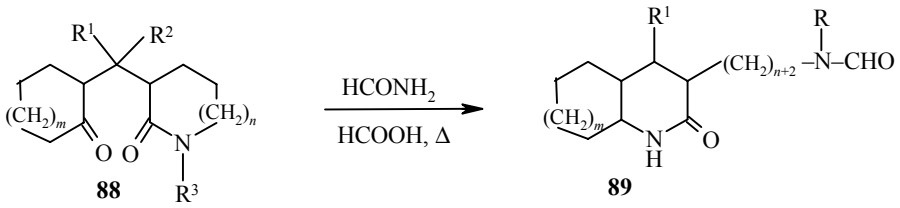
The β-cycloketols **36**, which are the products from intramolecular carbocyclization of the 1,5-diketones, are decyclized under the conditions of the Leuckart reaction and therefore form the same compounds as from the corresponding 1,5-diketones [31, 39, 115, 116]. The reaction mechanism remains debatable. Reduction of dihydropyridine by formic acid is also possible. For methylenedicyclohexanedione Colong [16] proposed the formation of the corresponding diformyl derivative of the diamine **87** as intermediate product.



With formamide (130-170°C) the semicyclic 1,5-diketones of types **29** and **30** form a mixture of the *cis* and *trans* isomers of perhydroquinolines [120]. From methylenebiscyclohexanone with the same reagent a mixture of the *trans-syn-trans* (α) and *trans-anti-cis* (β) stereoisomeric perhydroacridines is obtained [121, 122]. In the case of ethylidenebiscyclohexanone under the above-mentioned conditions

9-methylperhydroacridine was synthesized in the form of a mixture of the α-, β-, and γ-(*cis-syn-cis*) stereoisomers [123, 124]. It is also necessary to mention the alternative stereospecific method for the production of N-substituted perhydroacridines by the simultaneous action of an amine and potassium borohydride on methylenecyclohexanone [125, 126].

3-(ω-Aminoalkyl)hydroquinolones **89** were obtained from the substituted lactams **88** by the Leuckart reaction [127].



$m = 1$, $n = 2$, $R^1 = R^3 = Ph$, $R^2 = H$; $R^1 = Ph$, $R^2 = H$, $R^3 = PhCH_2$, $R^1 + R^2 = (CH_2)_5$, $R^3 = Ph$; $m = n = 1$, $R^1 = R^3 = Ph$, $R^2 = H$; $m = 2$, $n = 1$, $R^1 = R^3 = Ph$, $R^2 = H$; $m = n = 2$, $R^1 = R^3 = Ph$, $R^2 = H$

6. CATALYTIC HYDROAMINATION

In order to synthesize the difficultly obtainable saturated azaheterocycles of the piperidine, perhydroquinoline, and perhydroacridine series and related compounds extensive systemic investigations were carried out at Saratov State University on the catalytic hydroamination of aliphatic-aromatic, semicyclic, bicyclic, and other 1,5-diketones and the products from their intramolecular aldol carbocyclization. Metals of group VIII (Ni/Ru, Ru/C, Ni_{Ra}, RuO_2, and Pd/C) were used as catalysts. Ammonia, methylamine, aniline, and other alkyl- and arylamines and also ethanolamine, propanolamine, nitrobenzene, and certain nitro compounds were used as aminating agents. Catalytic amination was mainly realized at 100-150°C and in the case of RuO_2 even at 20-25°C. As a rule, the above-mentioned saturated azaheterocycles are formed during catalytic hydroamination; pyridinization only occurs in individual cases, or the corresponding diols are formed. The results of the catalytic hydroamination of 1,5-diketones were summarized by A. P. Krivenko and coauthors in a series of reviews and textbooks [128-132], and great attention was paid to the stereochemistry of saturated azaheterocycles of all the investigated series. This enabled us in the present work to omit a detailed analysis of the relationships and characteristics of the process and to refer the reader to other publications [128-132].

REFERENCES

1. C. Paul and C. Strasser, *Berichte*, **20**, 1889, 2576 (1887).
2. E. Knoevenagel and R. Weissgerber, *Berichte*, **26**, 436 (1893).
3. M. Scholtz, *Berichte*, **30**, 2295 (1897).
4. E. Knoevenagel and J. Fuchs, *Berichte*, **35**, 1788, 2848 (1902).
5. K. W. Merz and H. Richter, *Arch. Pharm.*, **275**, 294 (1937).
6. E. I. Orlov, *Zh. Russk. Fiz. Khim. Obshch.,* **38**, 1200 (1906).
7. E. Knoevenagel, *Liebigs Ann. Chem.*, **281**, 25 (1894).
8. P. Rabe and F. Elze, *Liebigs Ann. Chem.*, **332**, 18 (1904).
9. F. Muchael and W. Moller, *Liebigs Ann. Chem.*, **670**, 63 (1963).
10. D. Vorlender, *Liebigs Ann. Chem.*, **309**, 348 (1899).

11. G. Ya. Vanag, E. Ya. Gren, and E. I. Stankevich, *Izv. Vuzov. Khim. Khim. Tekhnol.*, **2**, 210 (1959).
12. G. Ya. Vanag and E. I. Stankevich, *Zh. Obshch. Khim.*, **30**, 3287 (1960).
13. H. Antake, *J. Chem. Soc.*, 2263 (1965).
14. F. Kröhnke, G. M. Ahrenholz, and K. F. Grosse, *J. Prakt. Chem.*, **11**, 256 (1960).
15. A. Peres de Carvalho, *Ann. Chim. (Roma)*, **4**, 449 (1935).
16. J. Colong, J. Dreux, and H. Deleplase, *Bull. Soc. Chim. France*, 447 (1957).
17. Imperial Chemical Industries Ltd, Belg. Patent 669512; *Chem. Abstr.*, **65**, 7153 (1966).
18. Neth. Pat. Appl. 6, 511861; *Chem. Abstr.*, **65**, 5446 (1966).
19. T. W. Whaley and D. G. Off, *J. Labell. Compounds and Radiopharm.*, **10**, 283 (1974); *Chem. Abstr.*, **81**, 135894 (1974).
20. T. D. Kazarinova, L. I. Markova, and V. G. Kharchenko, *Khim. Geterotsikl. Soedin.*, 511 (1990).
21. T. D. Kazarinova, L. I. Markova, and V G. Kharchenko, *Khim. Geterotsikl. Soedin.*, 647 (1994).
22. L. I. Markova and T. D. Kazarinova, in: V. G. Kharchenko (editor), *Nucleophilic Reactions of Carbonyl Compounds* [in Russian], Saratov (1985), p. 45.
23. T. D. Kazarinova, O. V. Litvinov, L. I. Markova, S. N. Chalaya, G. E. Marinicheva, and V. G. Kharchenko, *IV All-Union Conference on the Chemistry of Nitrogen-Containing Heterocyclic Compounds. Abstracts* [in Russian], Novosibirsk (1987), p. 61.
24. S. V. Dubovitskii, *Carbonyl Compounds in the Synthesis of Heterocycles. Abstracts* [in Russian], Saratov (1996), p. 136.
25. L. I. Donchak, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 239 (1975).
26. V. G. Kharchenko, S. N. Chalaya, and O. V. Litvinov, *Khim. Geterotsikl. Soedin.*, 352 (1985).
27. V. G. Kharchenko, S. N. Chalaya, L. K. Kulikova, and O. V. Litvinov, *Khim.-Farm. Zh.*, 824 (1987).
28. V. G. Kharchenko, S. N. Chalaya, O. V. Fedotova, and N. B. Pchelintseva, *Ninth Symposium on the Chemistry of Heterocyclic Compounds*, Bratislava (1987), p. 197.
29. N. V. Pchelintseva, S. N. Chalaya, and V. G. Kharchenko, *Zh. Org. Khim.*, **26**, 1904 (1990).
30. N. V. Pchelintseva, *Thesis for Candidate of Chemical Sciences* [in Russian], Saratov (1990).
31. M. N. Tilichenko and V I. Vysotskii, *Dokl. Akad. Nauk*, **119**, 1162 (1958).
32. V. I. Vysotskii and M. N Tichilenko, *Khim. Geterotsikl. Soedin.*, 751 (1965).
33. P. L. Frank and R. P. Seven, *J. Am. Chem. Soc.*, **71**, 2629 (1949).
34. F. Chubb, A. S. Hay, and R. B. Sandin, *J. Am. Chem. Soc.*, **75**, 6042 (1953).
35. M. N. Tilichenko, V. I. Vysotskii, and V. G. Kharchenko, *Uchenye Zapiski Saratovskogo Un-ta*, **71**, 159 (1959).
36. M. N. Tilichenko and V. G. Kharchenko, *Zh. Obshch. Khim.*, **32**, 1192 (1962).
37. L. Birkofer, S. M. Kirn, and H. D. Engels, *Chem. Ber.*, **95**, 1495 (1962).
38. V. G. Kharchenko, N. M. Kupranets, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, **13** (1968).
39. N. Barbulescu, F. Potmischil, and D. Romer, *Rev. Chim. (RSR)*, **21**, 677 (1970).
40. H. Essavy and A. A. Hamed, *Indian J. Chem.*, **16 B**, 880 (1978).
41. M. Weiss, *J. Am. Chem. Soc.*, **74**, 200 (1952).
42. S. Julia and D. Varech, *Bull. Soc. Chim. France*, 1127 (1959).
43. J. Colong, J. Dreux, and S. Thier, *Compt. Rend.*, **244**, 89 (1957).
44. T. D. Kazarinova, *Thesis for Candidate of Chemical Sciences* [in Russian], Saratov (1989).
45. L. I. Markova, T. D. Kazarinova, L. M. Yudovich, and V. G. Kharchenko, *Khim. Geterotsikl. Soedin.*, 209 (1990).
46. V. G. Kharchenko, L. I. Markova, T. D. Kazarinova, and L. M. Yudovich, *Khim. Geterotsikl. Soedin.*, 915 (1985).
47. L. V. Cherkesova and K. V. Mityurina, *Nucleophilic Reactions of Carbonyl Compounds. Abstracts* [in Russian], Saratov (1977), p. 68.

48. V. I. Vysotskii and T. V. Moskovkina, *Chemistry of Dicarbonyl Compounds. Abstracts* [in Russian], Zinatne, Riga (1986), p. 86.
49. D. A. Tsimbalenko, M. V. Skuratova, and O. V. Fedotov, *Contemporary Problems of Theoretical and Experimental Chemistry* [in Russian], Izd. SGU, Saratov (1999), p. 100.
50. V. A. Kaminskii, *Thesis for Doctor of Chemical Sciences* [in Russian], Vladivostok 1981.
51. P. Haas, *J. Chem. Soc.*, 189 (1961).
52. I. G. Erickson, *J. Am. Chem. Soc.*, **67**, 1382 (1945).
53. E. I. Stankevich and G. Ya. Vanag, *Izv. Akad. Nauk. LatvSSR. Ser. Khim.*, 223 (1961).
54. A. R. Katritzky and I. W. Suwinsky, *Tetrahedron*, **31**, 1549 (1975).
55. F. Wille and W. Sihab, *Monatsch. Chem.*, **108**, 929 (1977).
56. D. Craig, L. Schaefgen, and W. P. Tyler, *J. Am. Chem. Soc.*, **70**, 1624 (1948).
57. N. C. Cook and I. E. Lions, *J. Am. Chem. Soc.*, **87**, 3283 (1965).
58. A. N. Saverchenko, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 1232 (1972).
59. T. V. Zabolotnova, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 471 (1981).
60. S. A. Shumakov, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 109 (1990).
61. A. N. Saverchenko, Z. R. Bekkerova, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 243 (1974).
62. V. A. Kaminskii and M. N. Tilichenko, *Zh. Org. Khim.*, **5**, 186 (1969).
63. A. N. Saverchenko, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 384 (1973).
64. V. I. Vysotskii and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 376 (1971).
65. N. Barbulescu and F. Potmischil, *Rev. Roum. Chim.*, **15**, 1601 (1970).
66. N. Barbulescu and F. Potmischil, *Liebigs Ann. Chem.*, **735**, 132 (1970).
67. V. A. Kaminskii, A. N. Saverchenko, and M. N. Tilichenko, *Zh. Org. Khim.*, **6**, 404 (1970).
68. V. A. Kaminskii and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 1434 (1974).
69. V. I. Alekseev, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 235 (1975).
70. T. V. Moskovkina, V. A. Kaminskii, V. I. Alekseev, V. K. Gamov, and M. N. Tilichenko, *Chemistry of Carbonyl Compounds. Abstracts* [in Russian], Zinatne, Riga (1976), p. 101.
71. V. A. Kaminskii and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 1140 (1971).
72. L. N. Donchak, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 239 (1975).
73. V. A. Kaminskii, V. K. Gamov, L. M. Eremeeva, L. N. Donchak, A. N. Saverchenko, V. I. Alekseev, and M. N. Tilichenko, *Chemistry of Dicarbonyl Compounds. Abstracts* [in Russian], Riga (1981), p. 100.
74. L. M. Eremeeva, T. V. Moskovkina, Yu. V. Vasilenko, and A. N. Saverchenko, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 240 (1979).
75. V. A. Kaminskii, L. N. Donchak, and A. N. Saverchenko, in: V. G. Kharchenko (editor), *Nucleophilic Reactions of Carbonyl Compounds* [in Russian], Izd. SGU, Saratov (1982), p. 108.
76. L. N. Donchak, M. A. Zagoruiko, V. A. Kaminskii, and M. N. Tilichenko, *Carbonyl Compounds in the Synthesis of Heterocycles* [in Russian], Izd. SGU, Saratov (1996), p. 34.
77. O. Yu. Slabko, O. I. Britsina, and V. A. Kaminskii, *Khim. Geterotsikl. Soedin.*, 982 (1991).
78. V. A. Kaminskii, O. Yu. Slabko, and M. V. Gomolach, *Khim. Geterotsikl. Soedin.*, 927 (1990).
79. V. A. Kaminskii, O. G. Pestova, and L. V. Metennaya, *Khim. Geterotsikl. Soedin.*, 1495 (1992).
80. H. S. Broadbent, W. S. Burnham, R. M. Scheeley, and R. K. Olsen, *J. Heterocycl. Chem.*, **13**, 337 (1976).
81. E. Knoevenagel, *Berichte*, **36**, 2129, 2136, 218 (1903).
82. E. Knoevenagel, *Berichte*, **26**, 1085 (1893).
83. E. E. Bleise and M. Montagne, *Compt. Rend.*, **170**, 1760 (1925).
84. N. S. Gill, K. B. James, P. Lions, and R. T. Potts, *J. Am. Chem. Soc.*, **74**, 4923 (1952).
85. M. N. Tilichenko and G. V. Pavel', *Zh. Org. Khim.*, **1**, 1992 (1965).

86. G. A. Klimov and M. N. Tilichenko, USSR Inventor's Certificate 572455; *Byull. Izobr.*, No. 31, 29 (1977).
87. H. Stobbe and H. Volland, *Berichte*, **35**, 3973 (1902).
88. H. Stobbe, *J. Prakt. Chem.*, **86**, 210 (1912).
89. W. E. Hahn and J. Epzstain, *Rocz. Chem.*, **37**, 403 (1963).
90. M. N. Tilichenko, G. V. Pavel', and A. D. Chumak, *Zh. Org. Khim.*, **7**, 701 (1971).
91. M. N. Tilichenko, *Zh. Obshch. Khim.*, **25**, 2503 (1955).
92. L. S. Novikov, V. A. Mezentsev, and I. G. Tishchenko, *Khim. Geterotsikl. Soedin.*, 1693 (1979).
93. V. G. Kharchenko, L. I. Markova, T. D. Kazarinova, and L. M. Yudovich, *Khim. Geterotsikl. Soedin.*, 846 (1985).
94. V. G. Kharchenko, Yu. G. Struchkov, A. A. Espenbetov, L. I. Markova, and T. D. Kazarinova, *Khim. Geterotsikl. Soedin.*, 1085 (1987).
95. L. I. Markova, T. D. Kazarinova, L. M. Yudovich, and V. M. Kharchenko, *Khim. Geterotsikl. Soedin.*, 209 (1990).
96. B. D. Shaw, *J. Chem. Soc.*, 500 (1937).
97. N. Barbulescu, G. Baditse, and M. N. Tilichenko, *Zh. Obshch. Khim.*, **33**, 4027 (1963).
98. M. N. Tilichenko, *Uchenye Zapiski SGU*, **75**, 60 (1962).
99. A. Palsky, J. Hult, and J. Dreux, *Compt. Rend.*, 262, 1543 (1966).
100. V. M. Gamov, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 1525 (1974).
101. T. D. Kazarinova, L. I. Markova, and V. G. Kharchenko, *Khim. Geterotsikl. Soedin.*, 511 (1990).
102. V. G. Kharchenko, L. I. Markova, T. D. Kazarinova, and L. M. Yudovich, *Khim. Geterotsikl. Soedin.*, 846 (1985).
103. C. G. Oveberger and J. J. Monagle, *J. Am. Chem. Soc.*, **78**, 4470 (1956).
104. M. Lipp, F. Dallacker, and S. Munnes, *Liebigs Ann. Chem.*, **618**, 110 (1958).
105. L. N. Donchak, T. V. Zabolotnova, V. A. Kaminskii, and M. N. Tilichenko, *Chemistry of Dicarbonyl Compounds. Abstracts* [in Russian], Riga (1981), p. 69.
106. T. V. Moskovkina, V. A. Kaminskii, V. I. Vysotskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 826 (1973).
107. T. V. Moskovkina and M. N. Tilichenko, *Carbonyl Compounds in the Synthesis of Heterocycles* [in Russian], Izd. SGU, Saratov (1996), P. 31.
108. T. V. Moskovkina and E. V. Chebotkevich, in: V. G. Kharchenko (editor), *Nucleophilic Reactions of Carbonyl Compounds* [in Russian], Saratov (1985), p. 22.
109. T. V. Moskovkina and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 821 (1983).
110. T. V. Moskovkina, *XVI Mendeleev Congress of General and Applied Chemistry. Abstracts* [in Russian], St. Petersburg (1998), p. 216.
111. W. Schneider, *Liebigs Ann. Chem.*, **438**, 115 (1924).
112. A. T. Balaban, P. T. Frangopol, G. Matzescu, and C. D. Nenitzescu, *Bull. Soc. Chim. France*, 298 (1962).
113. A. T. Balaban, *Tetrahedron*, **26**, 739 (1970).
114. G. V. Pavel', M. V. Denisenko, and N. P. Bagrina, *Chemistry of Dicarbonyl Compounds. Abstracts* [in Russian], Riga (1981), p. 174.
115. M. N. Tilichenko and V. G. Kharchenko, *Zh. Obshch. Khim.*, **30**, 2283 (1960).
116. M. N. Tilichenko and V. G. Kharchenko, *Zh. Obshch. Khim.*, **29**, 2370 (1959).
117. V. A. Kaminskii, A. N. Saverchenko, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 1539 (1970).
118. L. M. Eremeeva, Yu. F. Vasilenko, V. A. Kaminskii, and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, 1361 (1977).
119. N. Sugimoto, *J. Chem. Soc. Jpn., Pure Chem. Sect.*, **64**, 192 (1944).
120. T. V. Moskovkina, M. N. Tilichenko, and V. N. Kurilenko, *Khim.-Farm. Zh.*, No. 7, 3 (1973).

121. N. Barbulescu and F. Potmischil, *Tetrahedron Lett.*, 5276 (1969).
122. N. Barbulescu and F. Potmischil, *Rev. Roum. Chim.*, **14**, 1427 (1969).
123. N. Barbulescu and F. Potmischil, *Tetrahedron Lett.*, 2309 (1969).
124. N. Barbulescu, F. Potmischil, and O. Romer, *Rev. Chim. (RSR)*, **21**, 451 (1970).
125. V. I. Vysotskii, *Zh. Org. Khim.*, **4**, 1494 (1968).
126. V. I. Vysotskii, *Khim. Geterotsikl. Soedin.*, 1236 (1970).
127. S. A. Shumakov and V. A. Kaminskii, *Khim. Geterotsikl. Soedin.*, 525 (1992).
128. A. P. Kriven'ko, T. G. Nikolaeva, and V. G. Kharchenko, *Khim. Geterotsikl. Soedin.*, 435 (1987).
129. A. P. Krivenko, P. V. Reshetov, and T. G. Nikolaeva, *Bashkir. Khim. Zh.*, **3**, 125 (1996).
130. T. G. Nikolaeva, P. V. Reshetov, and A. P. Kriven'ko, *Khim. Geterotsikl. Soedin.*, 867 (1997).
131. A. P. Kriven'ko and T. G. Nikolaeva, *Reductive Amination in the Synthesis of Azaheterocycles* [in Russian], Izd. SGU, Saratov (1991), p. 82.
132. A. P. Krivenko and T. G. Nikolaeva, *Chemistry of Five- and Six-Membered N,O-Containing Heterocycles* [in Russian], Saratov (1997), Chap. 10, p. 162.