SYNTHESIS OF HETEROCYCLES FROM AMINOAMIDE OXIMES[#]

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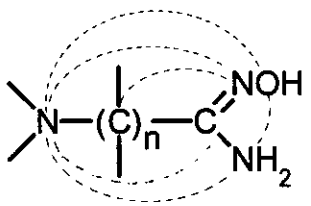
Abstract - Syntheses of nitrogen heterocycles starting from aminoamide oximes involving heterocyclic rearrangements including novel types of ring-chain tautomerism of pyrimidines are reviewed.

CONTENTS

[#] Submitted in the honour of the 65th birthday of Professor A. R. Katritzky

1. INTRODUCTION

Aminoamide oximes, easily obtainable from the reaction of aminonitriles with hydroxylamine, are versatile starting materials for the synthesis of various nitrogen heterocycles which are not at all, or not readily accessible by other methods. This review is restricted to syntheses in which one carbon atom is added in the ring forming process. This carbon atom is introduced by means of acylating agents (esters, carboxylic acid anhydrides, acyl chlorides), or aldehydes.



Ring formation utilizes only a few conventional methods such as condensation-hydrolysis, reduction, and various types of ring transformation. Although heterocyclic rearrangements are known since the 1900's, their systematic and thorough study has only been undertaken since the 1970's.[1-5]

The reason for the remarkable variety of *N*-heterocycles which can be synthesized from aminoamide oximes is the enhanced reactivity of the three hetero atoms of the amide oxime moiety, and in the case of mobile hydrogen the chain or the ring amino nitrogen atom. Moreover, in special cases the carbon atom of the amide oxime group and the α-carbon atom relative to the amide oxime moiety are also remarkably reactive. As there is no significant difference in the reactivity of the four hetero atoms competition among them becomes a decisive factor. Apart from substituents of amide oxime and the

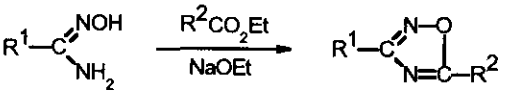
ring closure agent, reaction conditions and the thermodynamic stability of the products play also an important role. Often a single starting compound can be transformed with the same reagent into two, three, or occasionally even into four different heterocycles merely by changing reaction conditions. Competition of the four hetero atoms made also possible that a primary product formed in a fast reaction is converted to a second, or in some cases to a third and thermodynamically more stable ring system. Reductive ring transformation of the initially formed heterocycles opens the way to additional types of heterocycles.

2. REACTIONS OF AMINOAMIDE OXIMES WITH ACYLATING AGENTS

2.1 SYNTHESIS OF AMINO-1,2,4-OXADIAZOLES WITH CARBOXYLIC ESTERS

Tiemann and Krüger (1884) were first to synthesize 3,5-disubstituted 1,2,4-oxadiazoles by acylating the hydroxyl group of an amide oxime and followed subsequent dehydration,[6] this is still the most general method for the synthesis of 1,2,4-oxadiazoles.[7] The use of classical acylating agents (acid anhydrides, acyl halides), however, leads to difficulties when functional groups that can be acylated (*e.g.* hydroxyl, or amino) are present.[8-12]

Earlier a method has been developed for the synthesis of 1,2,4-oxadiazoles using carboxylic esters[13] (Scheme 1). This method can be safely employed for the selective ring closure of amide oximes containing primary, or secondary alkyl-, or arylamino functions.[14-16] Most of the amino-1,2,4-oxadiazoles reported in this review were synthesized by this method.



R^1 = aminoalkyl, aminoaryl, R^2 = alkyl, aryl

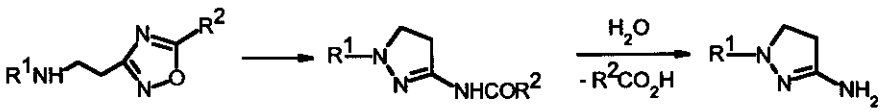
Scheme 1

2.2. TENDENCY OF AMINO-1,2,4-OXADIAZOLES TO UNDERGO RING TRANSFORMATIONS

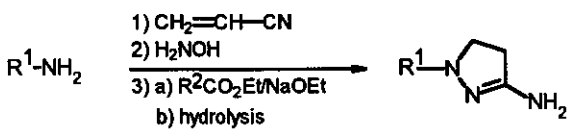
1,2,4-Oxadiazoles which have an amino moiety at the substituent at C-3, and at least one mobile hydrogen reveal a particularly high tendency to ring transformations.

2.2.1. A simple synthesis of 3-aminopyrazolines from primary amines:Ring transformation of 3-(2-aminoethyl)-1,2,4-oxadiazoles

3-(2-Aminoethyl)-1,2,4-oxadiazoles **(1)** readily rearrange in excellent yield to the isomeric, 3-acylaminopyrazolines **(2)**,[14,15] which give on hydrolysis 3-aminopyrazolines **(3)** (Scheme 2). All other reported methods[17] for the preparation of 3-aminopyrazolines utilized as precursors substituted hydrazines which generally are not readily accessible and often require special care. In contrast to these methods, in the oxadiazole rearrangement the formation of the N-N bond of the pyrazoline ring takes place as the last step of a simple three-step sequence starting from primary amines. This method can be regarded as entirely general.



1 **2** **3**

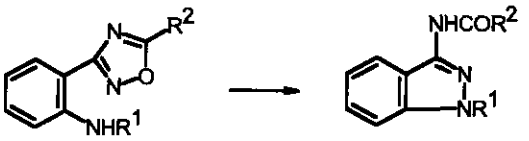


3

Scheme 2

2.2.2. Preparation of 3-aminoindazoles and hetero-fused 3-aminopyrazoles: Ring transformation of 3-(2-aminoaryl)-1,2,4-oxadiazoles

The isomerisation **1→2** was extended to 1,2,4-oxadiazoles in which the 2-aminoethyl side chain was replaced by 2-aminophenyl and 2-aminoheteroaryl groups, respectively. Using this method oxadiazoles **(4)** gave 3-acylaminoindazoles **(5)**,[12,16] and in a similar way various 3-acylaminopyrazoles condensed with pyrazole, pyridine, pyrazine, and pyrimidine rings were prepared[16,18,19] (Scheme 3).



4 5

Scheme 3

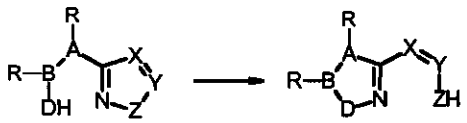
2.2.3. Extension of the second type Boulton-Katritzky scheme

For the interpretation of a large number of known azole-azole rearrangements Boulton, Katritzky *et al.* suggested two general schemes. The first one was proposed in 1964 for the ring transformation of a special group of bicyclic azoles in which crucial importance has been attributed to the π-electron system encompassing the reaction centre.[20] The second scheme was suggested in 1967 by Boulton, Katritzky, and Majid Hamid for the rearrangement of mononuclear azoles said to be analogous to the earlier type.[21] In the general scheme A, B, D, and X, Y, Z may denote C, N, O, and S atoms, respectively. The authors suggested that the continuous π-electron system extended over the reaction centre in the transition state is decisive in such processes, too [21-23] (Scheme 4).

The second Boulton-Katritzky scheme (1967)

Scheme 4

The scope of the Boulton-Katritzky rearrangements of the second type is very wide and was thoroughly reviewed by Ruccia *et al.*,[4] and recently by Vivona *et al.*[2] While the rearrangement **4→5** complies with the second Boulton-Katritzky scheme (Scheme 4),[21] the ring transformation **1→2**, however, is in conflict with this concept since here the side chain is saturated. Kinetic and thermodynamic studies as well as theoretical calculations established that both rearrangements (**4→5** and **1→2**) follow the same mechanism. The π-electron system of the parent azole ring, and the length of the side chain are crucial, whereas the saturation, or unsaturation of the latter are not decisive features for the success of the transformation. Therefore an extension of the second type Boulton-Katritzky scheme to azoles bearing a saturated side chain has been suggested[16,24-27,55] (Scheme 5).



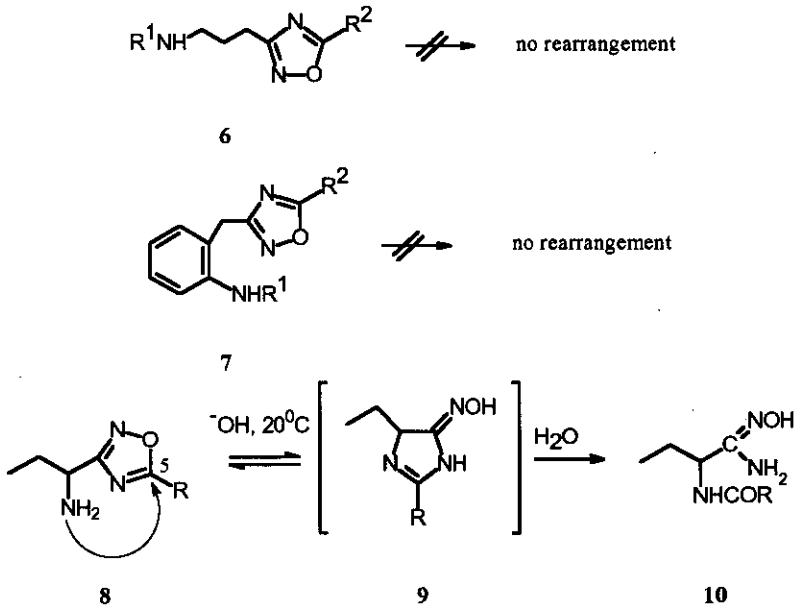
R=H, alkyl, *etc.*, or R+R = a single bond (π-bond between A and B)

The extended Boulton-Katritzky scheme

Scheme 5

2.2.4. Hydrolytic rearrangement of 5-substituted 3-(1-aminopropyl)- 1,2,4-oxadiazoles

In contrast to 3-(2-aminoethyl)-, and 3-(2-aminoaryl)-1,2,4-oxadiazoles (**1** and **4**) the deriva-tives with longer side chains, 3-(3-aminopropyl)- (**6**), and 3-(2-aminobenzyl)-1,2,4-oxadiazole (**7**) fail to undergo ring transformations, and show remarkable stability even under vigorous conditions[26,27] (Scheme 6). However, in dilute alkali at room temperature 3-(1-aminopropyl)-1,2,4-oxadiazoles (**8**) spontaneously transforms into α-acylaminobutyramide oximes (**10**) (Scheme 6). Most likely this is a multi-step reaction involving also a ring transformation in which the α-amino nitrogen establishes a bond with the C(5) atom of the 1,2,4-oxadiazole ring furnishing hydroxyimino-imidazole (**9**) hydrolysing finally to an amide oxime (**10**).[28]

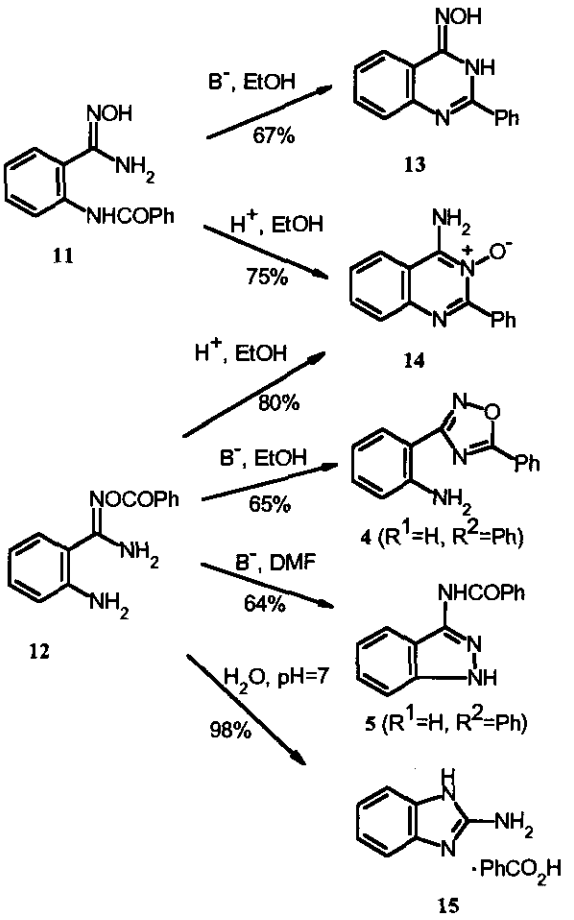


Scheme 6

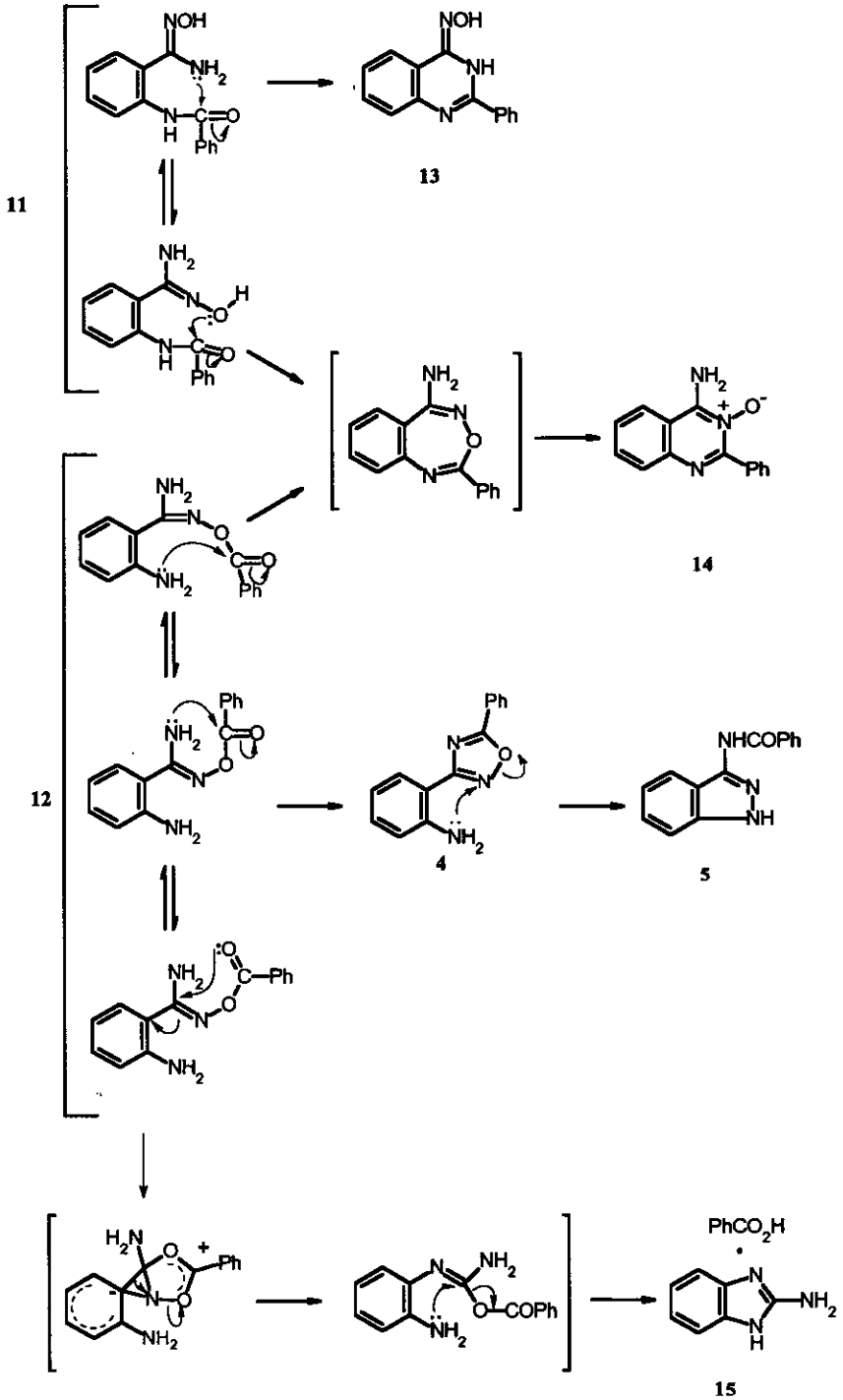
2.3 POSSIBLE PATHWAYS FOR THE TRANSFORMATION OF ACYLATED 2-AMINOBENZAMIDE OXIMES AND THEIR HETERO-ANALOGUES INTO 1,2,4-OXADIAZOLES, CONDENSED PYRIMIDINES, PYRAZOLES, AND IMIDAZOLES

The title acyl derivatives are of particular interest because owing to the competition among the nitrogen atoms of the amide oxime, the aromatic amino group, the oxygen atom of the oxime and that of the acyl group. They are highly versatile precursors of a variety of heterocycles.[18,19,29-33]

These possibilities are well illustrated by the *p*H and solvent dependent transformations of *N*-, and *O*-benzoyl derivatives of 2-aminobenzamide oxime **(11)** and **(12)** (Scheme 7).[34-36]



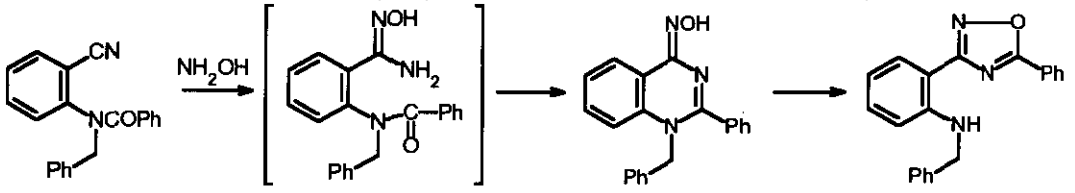
Scheme 7



Scheme 8

The interesting competition of the atoms involved in the ring formations is shown in Scheme 8. In the reactions **11**→**13**, and **12**→**4** the attack of the amino group of the amide oxime moiety is the main feature of the ring closure. In the reactions **12**→**14** and **4**→**5** the attacking group is the anilino amino group, while in the reaction **11**→**14** the oxime oxygen atom is responsible for the attack. Finally in the rearrangement **12**→**15**, the attack of the oxygen atom of the acyl group initiates ring closure. In the latter case a Beckmann rearrangement takes place in which the carbon atom of the amide oxime group, the oxime nitrogen, and the C(1) atom of the phenyl group are involved, followed by the attack of the aromatic amino group leading to the formation of 2-aminobenzimidazole (**15**). The practical importance of this reaction is that **15** can be prepared from anthranilonitrile in high yield in three simple steps (preparation of amide oxime, benzoylation, boiling in water).[34,35,37]

Interestingly the quinoidal 4-hydroxyiminoquinazoline (**18**) formed by ring closure of the intermediate amide oxime (**17**) prepared from the anthranilonitrile derivative (**16**) rearranges under hydrolytic conditions to the isomeric oxadiazole (**4**) by addition-elimination mechanism[37,38] (Scheme 9).



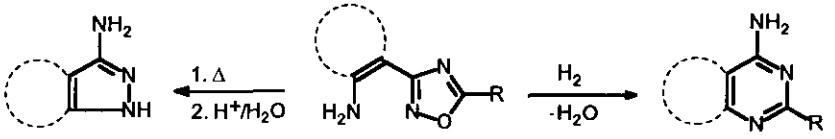
16 **17** **18** **4**

Scheme 9

2.4. REDUCTIVE RING TRANSFORMATIONS OF AMINO-1,2,4-OXADIAZOLES

2.4.1. Synthesis of 4-aminoquinazolines and hetero-fused 4-aminopyrimidines

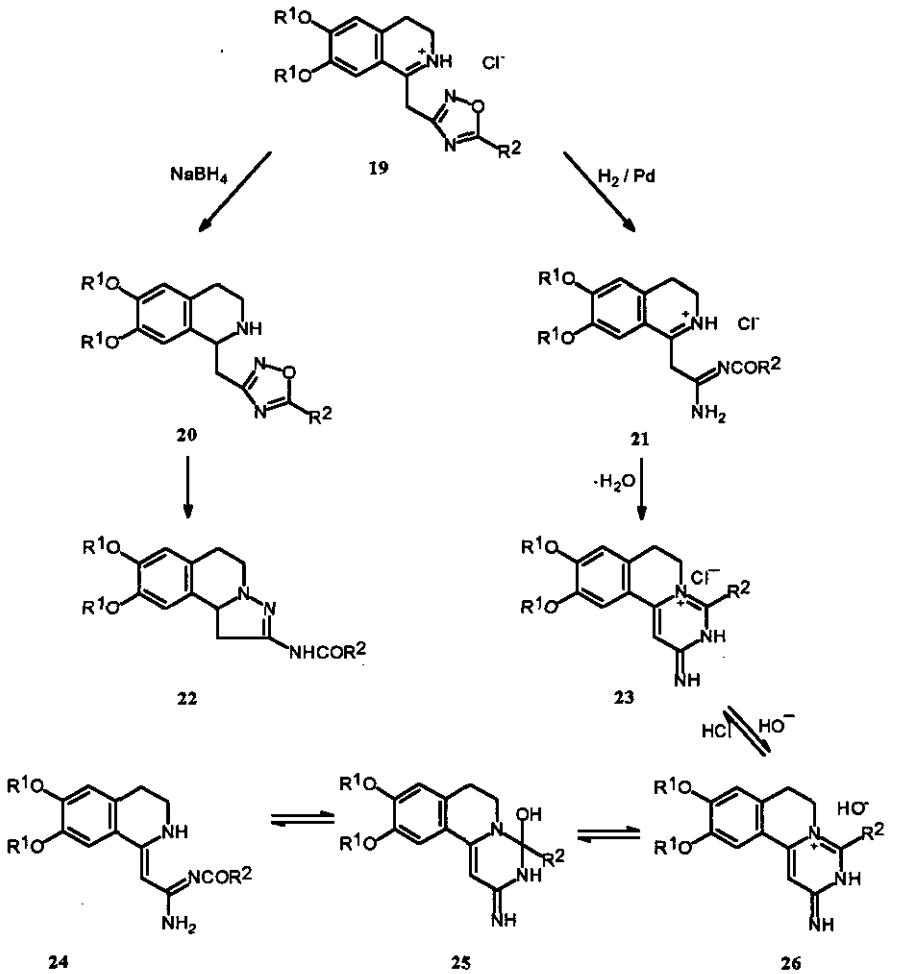
3-(2-Aminoaryl)-1,2,4-oxadiazoles which are the starting materials for 3-aminopyrazoles, too, (*cf.* 2.2.2.) by catalytic hydrogenation give condensed 4-aminopyrimidines. Several 4-amino-, or 4-iminoquinazolines, and 4-aminopyrimidines condensed with triazole, pyrazole, pyrimidine, and pyridine rings have been synthesized by this general method[39] (Scheme 10).



Scheme 10

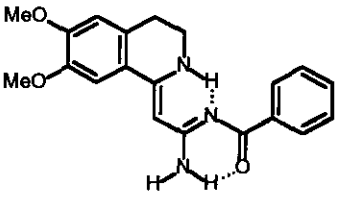
2.4.2 Formation and ring-chain tautomerism of pyrimido[6,1-a]isoquinoline-2-imines

The oxadiazole → pyrimidine reductive transformation method[39] has also been extended to the reduction of oxadiazolylmethylisoquinolines **(19)**, the heterocyclic analogues of dihydropapaverine which produces, depending on the reducing agent, regioselectively two different tricyclic heterocyclic compounds (Scheme 11). From **19** with sodium borohydride first the tetrahydroisoquinolines **(20)**, and then by the Boulton-Katritzky rearrangement pyrazolo[5,1-*a*]isoquinolines **(22)** were formed.[25] Catalytic hydrogenation of **19** caused the fission of the N-O bond thus furnishing acylamidines **(21)** which underwent in the acidic medium spontaneous ring closure giving pyrimido[6,1-*a*]isoquinolinium chlorides **(23)**[40]. Both methods are entirely general.



Scheme 11

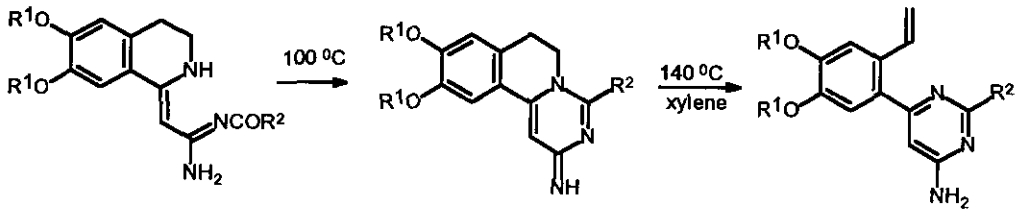
In basic medium the salts **(23)** form an equilibrium system consisting of three tautomeric forms of a pseudobase (**24** ⇌ **25** ⇌ **26**) of which **24** could be isolated. The relative stability of these compounds is explained by the low energy of the extended π-electron system and by two six-membered chelate rings also established by X-ray crystallography for one of the compounds[41] (R^1=Me, R^2=Ph).



Schematic representation of the intramolecular chelate rings in **24**

2.4.3. Preparation of 2,6-diaryl-4-aminopyrimidines: A novel olefin forming reaction

On heating at 100 °C the acylamidines **(24)** are transformed by loss of water into the anhydrobase **(27)** while refluxing in dry xylene at 140 °C they undergo a novel prototropic rearrangement *via* **27** to give 4-amino-6-(4,5-dialkoxy-2-vinylphenyl)-2-phenylpyrimidines, **(28)**[42] (Scheme 12). Related reactions have been described earlier, but in those instances a strong base was necessary.[43-45]

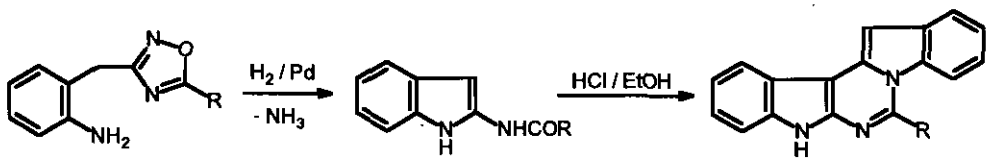


24 **27** **28**

Scheme 12

2.4.4. Formation of 2-benzoylaminoindole from 3-(2-aminobenzyl)-1,2,4-oxadiazole and its transformation into pyrimido[1,6-a:4,5-b']diindole

The catalytic reduction of **7** furnished 2-acylaminoindoles **(29)** by loss of ammonia. In the case of aroyl substituents attempted acid hydrolysis of **29** produced pyrimidodiindoles **(30)** (Scheme 13)[27].



7 29 30

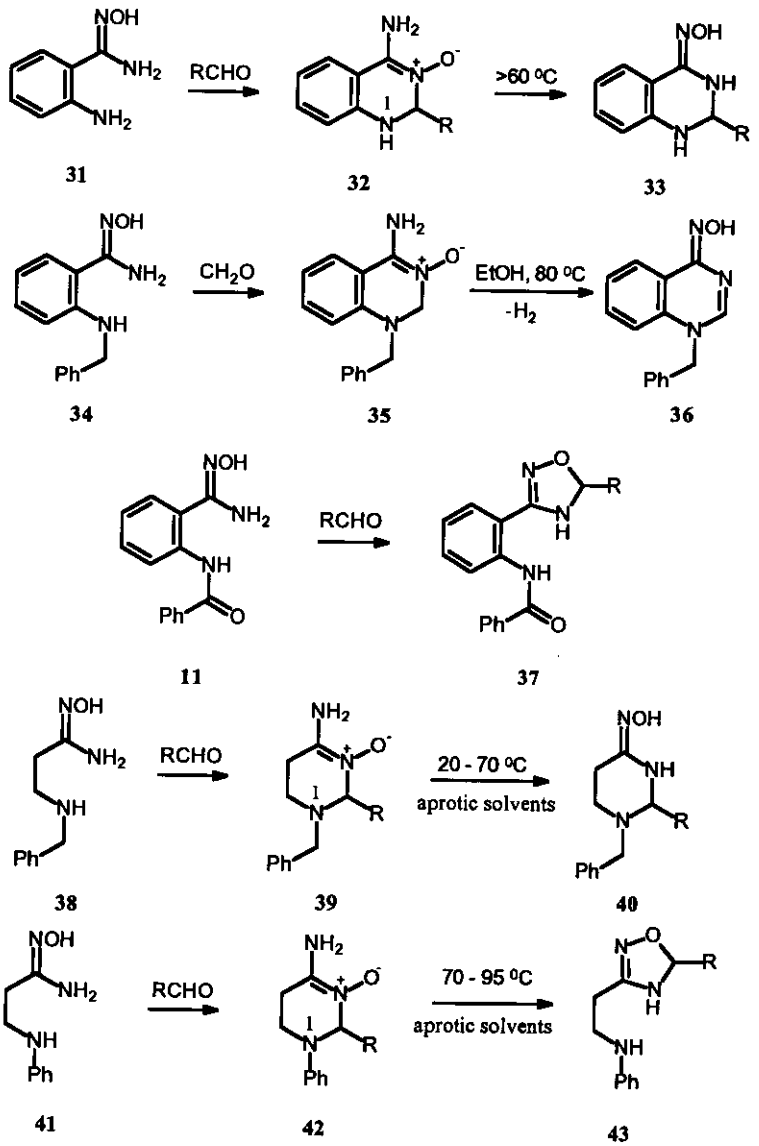
Scheme 13

3. REACTION OF β-AMINOAMIDE OXIME DERIVATIVES WITH ALDEHYDES

The reaction of aminoamide oximes with aldehydes shows in many aspects analogy with their acylation. Aldehydes react readily with both the amide oxime and amino groups to form either 1,2,4-oxadiazole or pyrimidine rings. Competitions between ring formations, subject to kinetic or thermodynamic control and secondary ring transformations are also characteristic for these reactions. The lower oxidation state of the reagent is manifested in the higher degree of saturation of the products. There is a characteristic difference in the reactivities of the amide oxime and amino moieties towards the two reagents. Although selectivity in acylations cannot be always achieved, it appears that acylating agents first attack the hydroxyl group of the amide oxime moiety, while aldehydes were found to react first with the alkyl-, or arylamino group. The reactions of aminoamide oximes with aldehydes has been at first studied by Gonçalves *et al.*[47-49]

3.1. FORMATION AND TRANSFORMATIONS OF PARTIALLY SATURATED 4-AMINOPYRIMIDINE-3-OXIDES

The reaction of aldehydes with benzamide oximes having a primary or secondary amino group in position 2 of the phenyl group, as well as with propionamide oximes with a secondary amino group in β-position furnished 4-aminopyrimidine-3-oxides.[48,50-52] If the amino group is acylated, the corresponding 4,5-dihydro-1,2,4-oxadiazoles are formed[50] (Scheme 14).



Scheme 14

The initially formed *N*-oxides readily undergo various rearrangements, presumably by different mechanisms. Reaction of 2-aminobenzamide oxime **(31)** with aldehydes at room temperature gave 4-amino-quinazoline-3-oxides **(32)** which isomerized to oximes **(33)** over 60°C. This interesting Dimroth rearrangement takes place in aprotic solvents, too.[51] The important role of the mobile

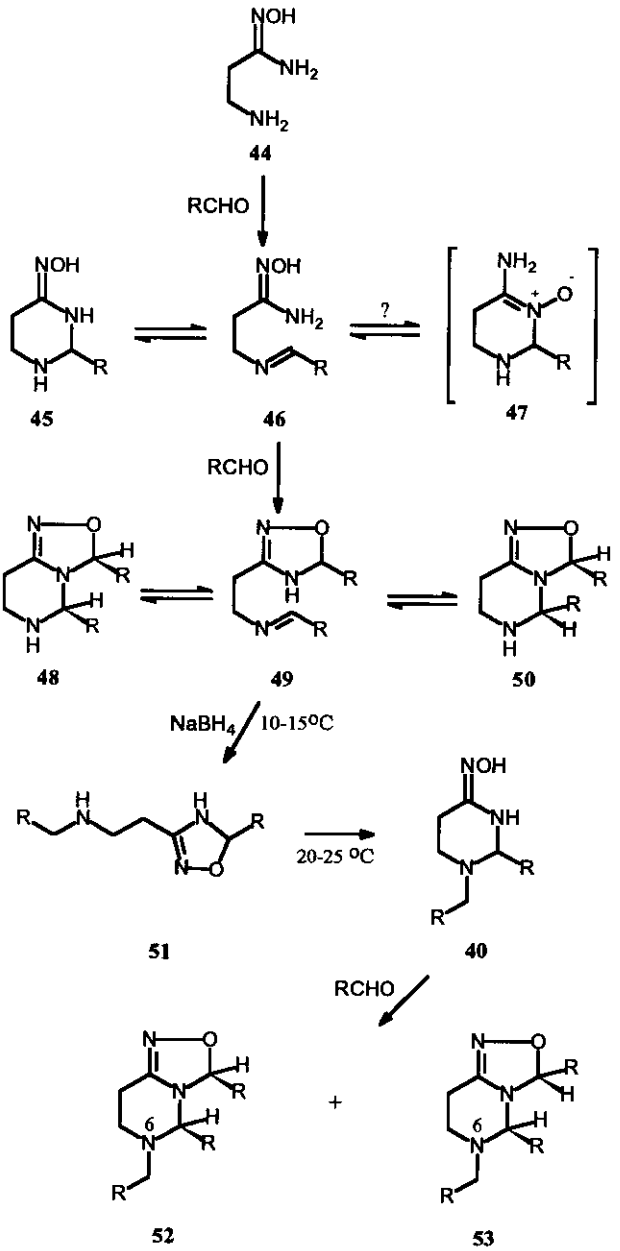
hydrogen at N(1) atom in **32** is indicated by the fact that the *N*-benzyl derivative **(35)** is stable in aprotic solvents, in protic solvents, and in the presence of air, however, an oxidative rearrangement takes place producing the novel quinoidal 4-hydroxyiminoquinazoline **(36)**, most likely by an addition-elimination mechanism.[51] However, the pyrimidine-3-oxides **(39)** and **(42)** rearrange in aprotic solvents. It is remarkable in these cases how the N(1) substituent of the parent *N*-oxides determines the structure of the products. Compound **(42)** containing electron withdrawing substituent rearranges to the isomeric anilino-ethyloxadiazoline **(43)**,[50] whereas the compound with benzyl substituent gives 4-hydroxyimino-hexahydropyrimidine **(40)**.[52]

3.2 FORMATION AND RING-CHAIN TAUTOMERISM OF 4-HYDROXYIMINO-HEXAHYDROPYRIMIDINE DERIVATIVES

In contrast to the former reactions (Scheme 14) in the case of 3-aminopropionamide oxime **(44)** containing a primary amino group (which can be regarded as the parent compound of β-aminoamide oximes), the formation of 4-aminopyrimidine-3-oxides has never been detected. With one equivalent of benzaldehyde, or its derivatives bearing electron withdrawing substituents imines **(46)** were formed which equilibrate in aprotic solutions with pyrimidines **(45)**. Both forms can be isolated pure and interconverted in solution. In contrast, in the case of cinnamaldehyde and benzaldehydes containing electron releasing substituents only the open-chain imine tautomer could be detected both in solution and in the solid state[49,53] (Scheme 15).

Reaction of **44** with two equivalents of benzaldehyde, or substituted benzaldehyde gives *cis*-5,6,7,8-tetrahydro-3,5-diaryl-3*H*-[1,2,4]oxadiazolo[4,3-*c*]pyrimidines **(48)**, first members of a new heterocyclic ring system. According to ^{1}H-, ^{13}C-, and ^{15}N-nmr studies these compounds form in solution a triple tautomeric equilibrium comprising the bicyclic forms **48** and **50** further the open chain 3-[2-(benzylideneamino)ethyl]-5-aryl-4,5-dihydro-1,2,4-oxadiazoles **(49)**.[54] No example has been found for such an *endo*-type triple tautomeric system involving amine addition to a C=N bond which can be regarded as the nitrogen-heterocyclic analogue of the mutarotation of sugars. Treating the equilibrium mixture with sodium borohydride gives aminoethyloxadiazoline **(51)** which readily rearranges to hydroxyiminohexahydropyrimidine **(40)**. Reaction of the latter with aldehydes gives the 1:1 mixture of the *cis* and *trans* oxadiazolo[4,3-*c*]pyrimidines **(52)** and **(53)**. As in these compounds no

mobile hydrogen is attached to N(6), there is no possibility for tautomerism, and both forms could be isolated in crystalline form (Scheme 15)[55].



Scheme 15

4. CONCLUSIONS

Aminoamide oximes smoothly obtained by the reaction of aminonitriles with hydroxylamine are versatile synthons for the straightforward syntheses of different types of amino substituted heterocycles. The variety of compounds obtained with acylating agents and aldehydes indicates the wide scope of this synthons, and it is very likely that with other reagents they can be exploited for the syntheses of many other heterocycles.

5. REFERENCES

1. A. R. Katritzky, M. F. Gordeev, *Heterocycles*,1993, **35**, 483.
2. N. Vivona, S. Buscemi, V. Frenna, and G. Cusmano, `Advances in Heterocyclic Chemistry: Ring Transformation of Five-Membered Heterocycles` Vol. 56., ed. by A. R. Katritzky, Academic Press, Inc. London, 1993, pp. 49-154 and references cited therein.
3. G. L'abbé, *J. Heterocycl. Chem.*, 1984, **21**, 627.
4. M. Ruccia, N. Vivona, and D. Spinelli, Advances in Heterocyclic Chemistry: `Mononuclear Hetrocyclic Rearrangements` Vol. 29., ed. by A. R. Katritzky and A. J. Boulton, Academic Press Inc., London, 1981, pp. 141-169.
5. H. C. Van der Plas, *Ring Transformations of Heterocycles,* Vols. 1, 2. Academic Press, Inc. London, 1973.
6 F. Tiemann and P. Krüger, *Ber.*, 1884, **17**, 1685.
7 F. Eloy and R. Lenaers, *Chem. Rev.*, 1962, **62**, 155.
8. L. B. Clapp, Advances in Heterocyclic Chemistry: `1,2,4-Oxadiazoles` Vol. 20, ed. by A. R. Katritzky, and A. J. Boulton, Academic Press, Inc., London 1976, p. 65-116.
9. S. Chion and H. J. Shine, *J. Heterocycl. Chem.*, 1989, **26**, 125.
10. H. Gonçalves and A. Secches, *Bull. Soc. Chim. France* 1970, 2589.
11. Hoffmann - LaRoche A.G. (Inv. J. M. Osbond, P. G. Philpott) *Ger. Offen. 1,946,829* (6. May. 1970) (Chem. Abstr.,*1970*, **73**, P25483e).
12. N. Vivona, G. Cusmano, G. Macaluso, V. Frenna, and M. Ruccia, *J. Heterocycl. Chem.*, 1979, **16**, 783.
13. K. Harsányi, P. Kiss, D. Korbonits, and I. Malyáta, *Arzneim.-Forsch.*, 1966, **16**, 215.
14. D. Korbonits, E. M. Bakó, and K. Horváth, *J. Chem. Res. (S)*, 1979, 64.
15. D. Korbonits, E. M. Bakó, and K. Horváth, *J. Chem. Res.(M)*, 1979, 0801.

16. D. Korbonits, I. Kanzel-Szvoboda, and K. Horváth, *J. Chem. Soc., Perkin Trans. 1.* 1982, 759.

17. J. Elguero, in 'Comprehensive Heterocyclic Chemistry: Pyrazoles and Their Benzo Derivatives', vol. 5, ed.by A. R. Katritzky and C. W. Rees, Pergamon Press, New York, London, Sydney, 1984, pp. 169-303.

18. M. Kocevar, M. Tišler, and B. Stanovnik, *Heterocycles,* 1982, **19,** 339.

19. B. Vercek, I. Leban, B. Stanovnik, and M. Tišler, *J. Org. Chem.*, 1979, **44,** 1695.

20. A. J. Boulton, P. G. Ghosh, and A. R. Katritzky, *Angew. Chem.*, 1964, **76,** 816.

21. A. J. Boulton, A. R. Katritzky, and A. Majid Hamid, *J. Chem. Soc. (C)*, 1967, 2005.

22. A. J. Boulton, *Lect. Heterocycl. Chem.*, 1974, **2,** 45.

23. A. Sultan Afridi, A. R. Katritzky, and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, 1976, 315.

24. K. Horváth, D. Korbonits, G. Náray-Szabó, K. Simon, *J. Mol. Struct. (Theochem),* 1986, **136,** 215.

25. I. Bata, G. Héja, P. Kiss, and D. Korbonits, *J. Chem. Soc., Perkin Trans. 1*, 1986, 9.

26. D. Korbonits, K. Horváth, Cs. Gönczi, and J. Tamás, *Acta Chim. Acad. Sci. Hung.*, 1984, **117,** 239.

27. I. Bata, D. Korbonits, P. Kolonits, B. Podányi, and T. Takácsy-Erős, K. Simon, *Chem. Ber.*, 1993, **126,** 1835.

28. E. M. Bakó, K. Horváth, E. Pálosi, and D. Korbonits, *Chem. Ber.*, 1988, **121,** 723.

29. B. Stanovnik, U. Urleb, and M. Tišler, *Heterocycles*, 1985, **23,** 2819.

30. M. Kocevar, B. Stanovnik, and M. Tišler, *J. Heterocycl. Chem.*, 1982, **19,** 1397.

31. M. Kocevar, B. Stanovnik, and M. Tišler, *Tetrahedron*, 1983, **39,** 823.

32. H. Gonçalves, F. Mathis, and C. Foulcher, *Bull. Soc.Chim. France*, **1970,** 2599.

33. N. V. Abbakumova, Yu. G. Putsikin, Yu. A. Baskakov, and Yu. A. Kondratiev, *Zh. Geterotsikl.Soedin.*, **1981,** 1264.

34. D. Korbonits and P. Kolonits, *J. Chem. Res.(S)*, **1988,** 209.

35. D. Korbonits and P. Kolonits, *J. Chem. Res.(M),* **1988,** 1652.

36. D. Korbonits and P. Kolonits, *Acta Chim. Hung.*, 1990, **127,** 795.

37. D. Korbonits, I. Kanzel-Szvoboda, Cs. Gönczi, K. Simon, and P. Kolonits, *Chem. Ber.*, 1989, **122,** 1107.

38. A. E. Moormann and D. F. Flynn, *13th Int. Congr. Heterocyclic Chem.*, Oregon, Aug. 1991, Abstr. P02-68.

39. D. Korbonits, P. Kiss, K. Simon, and P. Kolonits, *Chem. Ber.*, 1984, **117,** 3183.

40. D. Korbonits, P. Kiss, I. Bata, G. Héja, K. Simon, and P. Kolonits, *Chem. Ber.*, 1987, **120,** 1039.

41. D. Korbonits, G. Horváth, P. Kiss, K. Simon, and P. Kolonits, *Chem. Ber.*, 1990, **123,** 493.

42. D. Korbonits, K. Simon, and P. Kolonits, *Chem. Ber.*, 1991, **124**, 111.

43. B. Lal, R. M. Gidwani, and N. J. de Souza, *J. Org. Chem.*, 1990, **55**, 5117.

44. T. Kametani, T. Honda, T. Sugai, and K. Fukumoto, *Heterocycles*, 1976, **4**, 1927.

45. T. Kametani, T. Sugai, Y. Shagi, T. Honda, F. Satoh, and K. Fukumoto, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1151.

46. H. Gonçalves and J. Barrans, *C. R. Acad. Sci. Paris*, 1964, **258**, 3507.

47. H. Gonçalves and M. Bon, *C. R. Acad. Sci. Paris*, 1975, **280**, 141.

48. H. Gonçalves, C. Foulcher, and F. Mathis, *Bull. Soc. Chim. France*, 1970, 2615.

49. H. Gonçalves, F. Mathis, and J. Barrans, *Bull. Soc. Chim. France*, 1967, 2321.

50. D. Korbonits, K. Simon, and P. Kolonits, *Tetrahedron Lett.*, 1983, **24**, 5763.

51. D. Korbonits and P. Kolonits, *J. Chem. Soc., Perkin Trans. 1.*, 1986, 2163.

52. D. Korbonits, E. Tóbiás-Héja, K. Simon, and P. Kolonits, *Liebigs Ann. Chem.*, in the press

53. D. Korbonits, E. Tóbiás-Héja, and P. Kolonits, *Chem. Ber.*, 1991, **124**, 1199.

54. D. Korbonits, E. Tóbiás-Héja, K. Simon, and P. Kolonits, *Chem. Ber.*, 1991, **124**, 2065.

55. D. Korbonits, E. Tóbiás-Héja, K. Simon, Gy. Kramer, and P. Kolonits, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3069.

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