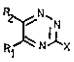
In order to investigate the generality of this mechanism in the 1,2,4-triazine series, we extended our amination studies to some derivatives containing different leaving groups at C-3 and various substituents at C-5 or C-6 of the triazine ring (see Figure).



1. X = F R$_1$ = Ph R$_2$ = H
2. X = Cl R$_1$ = Ph R$_2$ = H
3. X = Br R$_1$ = Ph R$_2$ = H
4. X = J R$_1$ = Ph R$_2$ = H
5. X = OCH$_3$ R$_1$ = Ph R$_2$ = H
6. X = SCH$_3$ R$_1$ = Ph R$_2$ = H
7. X = SO$_2$CH$_3$ R$_1$ = Ph R$_2$ = H
8. X = +N(CH$_3$)$_3$ R$_1$ = Ph R$_2$ = H
9. X = Cl R$_1$ = *t*-Bu R$_2$ = H
10. X = OCH$_3$ R$_1$ = *t*-Bu R$_2$ = H
11. X = SCH$_3$ R$_1$ = *t*-Bu R$_2$ = H
12. X = SO$_2$CH$_3$ R$_1$ = *t*-Bu R$_2$ = H
13. X = +N(CH)$_3$ R$_1$ = *t*-Bu R$_2$ = H
14. X = Cl R$_1$ = H R$_2$ = Ph
15. X = SCH$_3$ R$_1$ = H R$_2$ = Ph
16. X = Cl R$_1$ = Ph R$_2$ = Ph
17. X = OCH$_3$ R$_1$ = Ph R$_2$ = Ph
18. X = SCH$_3$ R$_1$ = Ph R$_2$ = Ph
19. X = SO$_2$CH$_3$ R$_1$ = Ph R$_2$ = Ph
20. X = +N(CH)$_3$ R$_1$ = Ph R$_2$ = Ph

It was found that besides the corresponding 3-amino compounds as main product, several by-products are formed depending on the nature of the substituents on positions 3 and 5.

With the compounds **2**, **3** and **4** a considerable amount of 2,4-diphenyl-1,3,5-triazine is obtained as by-product together with some of the dehalogenated product 5-phenyl-1,2,4-triazine.

With compound **6**, ring contraction into 3-methylthio-5-phenyl-1,2,4-triazole takes place as side reaction.

It has been proved using the corresponding [4-^{15}N]triazines that the formation of the 3-amino compounds occurs by a ring opening - ring closure sequence (S$_N$ANRORC) and/or by the more classical addition-elimination mechanism (S$_N$AE). As proved by nmr spectroscopy the addition of the amide ion to C-5 in 3-X-triazines is more favoured than addition to C-3. However, in cases where a substituent is present at C-3 which has highly electron-attracting properties [+N(CH$_3$)$_3$, SO$_2$CH$_3$], the addition to C-3 is the favourite process. The mechanism of the amination and the ring modifying process will be discussed.

REFERENCES

1. A. RYKOWSKI, H. C. von der PLAS, Rec. Trav. Chim. 94, 204 (1975).

LE .I 20

SOME NOVEL TYPE ELECTRON DEFICIENT HETEROAROMATIC AMMONIOAMIDATES

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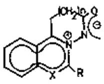
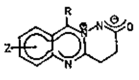
We wish to report on the synthesis of novel type electron deficient heteroaromatic ammonioamidates derived by incorporation of the amidate nitrogen and carbon and of the ammonio nitrogen atoms into a second ring (Compounds **1**, **2**, **3**).

They key step of the syntheses is based on neighboring-group participation of the nitrogen atom of the starting heteroaromatic system in the cleavage of acyl azide groups.



X = CH 1
X = N 2



3

The structures of **1**, **2** and **3** were proved by spectroscopical means and by unambiguous syntheses.

The tautomerism and photochemical behaviour of **1—3** were also investigated.

LE I 21

THE CONDENSATION OF o-AMINOBENZALDEHYDE WITH PYRAZOLE-5-ONES

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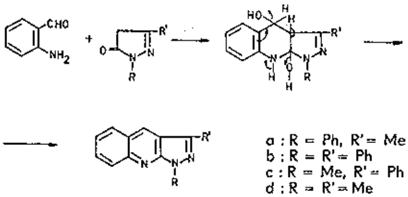
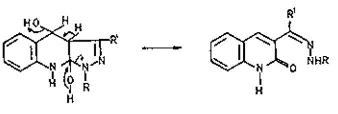
The Friedländer quinoline synthesis was extended to the condensation of o-aminobenzaldehyde with pyrazole-5-one and its derivatives (1a — 1i) in order to obtain pyrozoloquinolines (3)



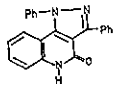
a : R = Ph, R' = Me
b : R = R' = Ph
c : R = Me, R' = Ph
d : R = R' = Me
e : R = H, R' = Ph
f : R = H, R' = Me
g : R = Ph, R' = H
h : R = Me, R' = H
i : R = R' = H

This could be achieved only in few cases. The behavior of the intermediary compound (2) depends on the electronic properties of both the R and R' substituents. When the pyrazole-5-one is not stabilized by R' = Ph the pyrazole moiety in the intermediary compound (2) is cleaved and corresponding hydrazones of 1-H-3-acylquinoline-2-one (4) are formed apart from other products.

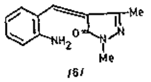


(2) (4)

In the case of 1,3-diphenylpyrazole-5-one (1b) pyrazoloquinoline(5) is also formed by the intramolecular Michael-type addition and subsequent oxidation. 1,3-Dimethylpyrazole-5-one (1d) is much more resistant towards condensation and the major product formed was 1,3-dimethyl-4-(o-aminobenzylidene) pyrazole-5-one (6).

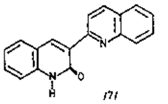


(5)

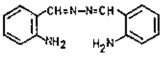


(6)

Moreover, both hydrazones (4a) and (4d) undergo condensation with o-aminobenzaldehyde yielding 3-(2-quinolyl)quinolin-2-one (7). Also benzylidenepyrazole-5-one (6) turns into both pyrazoloquinoline (3d) and quinolylquinoline-2-one (7). 1-H-Pyrazole-5-ones (1f) and (1i) which are not stabilized with R' = Ph can be a source of hydrazine. The latest is formally liberated from pyrazole-5-ones yielding with o-aminobenzaldehyde 2,2'-diaminobenzaldazine (8).

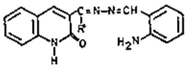


(7)



(8)

Corresponding both 3-benzoyl- and 3-formyl-1-H-quinoline-2-ones (4e) and (4i) are also formed, however, they undergo condensation with o-aminobenzaldehyde to give azines (9e) and (9i), respectively.



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LE I 22

REACTION WITH AROYLIMIDODITHIOCARBONATE

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Abstract — This paper is dealing with the reaction between aroyl-aminodithiocarbomates and alkylating reagents forming aroyl-imidodithiomethylcarbonate 1 and -thiazoles.

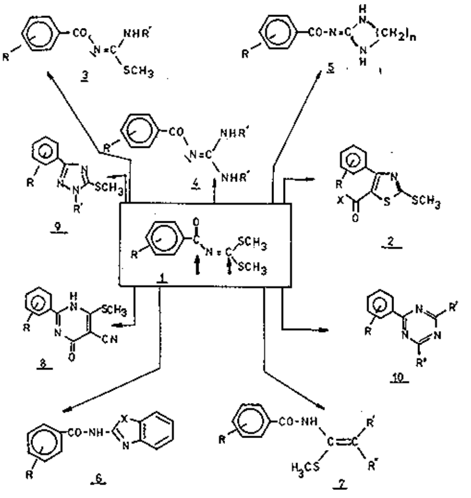
The reactivily of these compounds have been investigated.

Reaction of 1 with nucleophilic compounds gives new possibilities of synthesizing heterocycles.

With ammonia, aliphatic and aromatic amines 1 yields subst. isothioureas and subst. guanidines. ^{1}H-NMR spectra of these compounds are interpreted as to their E/Z isomerism and their imine-enamine tautomerism. Reaction of 1 with diamines and aromatic amines, respectively, which still have a nucleophilic substituent in ortho-position next to the amino group leads to the heterocycles. The reaction 1 with CH-acid compounds leads to acylthioamides, with cyanacetamide to the pyrimidone, and with hydrazines, guanidines or thioamides to the heterocycles 1,2,4-thiazole and 1,3,5-triazines.

The mass-, IR- and ^{1}H-NMR spectra of the synthesized compounds are discussed.

Schema



LE II 1

THE OXIDATION OF PYRIDINES WITH COPPER SULFATE

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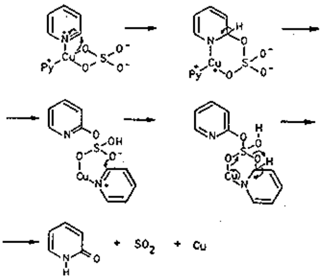
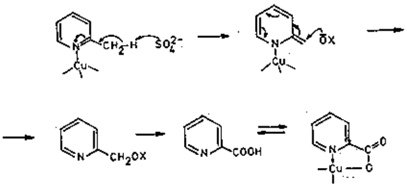
Oxidation of pyridine, 3-picoline, 3,5-lutidine, quinoline, isoquinoline and acridine with hydrated copper sulfate gives the corresponding pyridones probably via the intramolecular reaction of a base — Cu (II) complex:



The homologues of pyridine bearing the methyl groups in the α- and γ- positions undergo demethylation. The reaction goes via the aldehyde and carboxylic acid formation. Picolinic acid could be isolated after oxidation of 2-picoline owing to the formation of a relatively stable copper chelate. Also 1,2-bis (3-methyl-4-pyridyl)ethylene is formed with a low yield from 3,4-lutidine. Oxidation of the α- and γ- methyl groups may be taking place via the hydrogen — abstraction from the side-chain.



The unusual oxidation of not only the α- but also the β-carbon atom in 2- and 4- ethylpyridines has been discovered. Apart from pyridine also 2- and 4-picolines are formed. As far as we are aware this is the only example known of such an oxidation at the terminal atom of a side chain, containing more than one carbon atom. A radical process seems likely to be involved in this case.

LE II 2

NEW REARRANGEMENTS OF N-CONTAINING RINGS

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